Pergamon

TETRAHEDRON

Tetrahedron 56 (2000) 4085–4094

Phthalocyanine-related Macrocycles: Cross Cyclotetramerisation Products from 3,4-Dicyanothiophenes, 2,3-Dicyanothiophene and 3,6-Dialkylphthalonitriles

Michael J. Cook* and Ali Jafari-Fini

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Received 25 February 2000; revised 23 March 2000; accepted 13 April 2000

Abstract—Examples of the novel tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine and tribenzo[b,g,l]thiopheno[2,3-q]porphyrazine ring systems have been obtained by cross cyclotetramerisation reactions of 3,6-dialkylphthalonitriles with 3,4-dicyanothiophenes and 2,3-dicyanothiophene respectively. Dibenzodithiopheno[2,3]porphyrazines and benzotrithiopheno[2,3]porphyrazines have also been recovered. Octaoctyl tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine, in particular, shows a strongly split Q-band absorption in the far red region of the spectrum, one component of which is highly bathochromically shifted relative to the corresponding band in octaoctyl phthalocyanine. The compounds, most of which exhibit columnar liquid crystal behaviour, form even, transparent spin-coated films which exhibit a broad band absorption envelope, in some instances extending from 600 nm to beyond 800 nm. Reaction of 2,3-dicyanothiophene with a 2,5-dialkyl-3,4-dicyanothiophene, the latter in excess, gives a product mixture rich in macrocycles derived predominantly from involvement of the former.

Introduction

Phthalocyanines (Pcs), unmetallated and metallated, contain a cyclic 18π electron system which provides the basis for a large number of their unique properties.[1] The characteristic bright blue/green colour of these macrocycles originates from an intense narrow band absorption in the visible region of the spectrum, the Q-band, and has led to their extensive use as commercial dyes and pigments. However, there is also much interest in their redox properties, conductivity and photoconductivity for applications within a variety of devices[2] and their photophysical properties render some of them promising as singlet oxygen photosensitizers in photodynamic therapy.[3] Distortion of the cyclic π electron system induced by lowering the symmetry of the macrocyclic system tunes or enhances certain photophysical properties. The Q-band absorption may show substantial splitting and the introduction of push–pull substituent effects are of interest in NLO studies.[4] Examples of so-called 3:1 Pcs, in which three of the benzenoid rings bear one type of substituent and the fourth a second type, have been demonstrated to exhibit both second and third harmonic generation.[5]

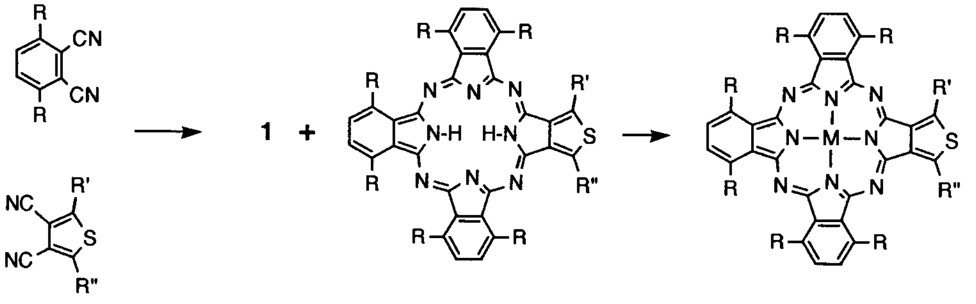
More elaborate 3:1 structures include those in which one of the four benzenoid rings in the phthalocyanine structure is further benzoannellated, as exemplified by Kobayashi et al.[6] They reacted a subphthalocyanine with both a benzo- and naphtho-fused diiminoisoindoline to give 3:1 macrocycles with three benzenoid rings and either a naphthalene or anthracene ring in the fourth quarter of the molecule. The replacement of benzenoid rings by heteroaromatic rings offers an alternative type of perturbation of the 18 π electron system and, where appropriate, the opportunity to develop chemistry at the heteroatom. However, 3:1 macrocycles containing just one heteroaromatic ring in place of a benzenoid ring have as yet received little attention. Van Lier and coworkers[7] successfully incorporated a pyrazine and a quinoxaline unit by ring expansion of a subphthalocyanine while Shibamiya and coworkers[8] have investigated cross reactions of phthalic anhydride and pyridine carboxylic acid anhydrides. Recently we reported examples of hexaalkyl substituted derivatives of tribenzopyridino[3,4]porphyrazine[9] and heptaalkyl derivatives of tribenzoimidazolo[3,4]porphyrazine,[10] macrocycles obtained by cross cyclotetramerisation of a 3,6-dialkylphthalonitrile with 3,4-dicyanopyridine and 1-alkyl-4,5-dicyanoimidazoles respectively. The alkyl substituents promote columnar liquid crystal properties akin to those exhibited by octaalkyl phthalocyanine derivatives of type **1**.[11] They also confer solubility in organic solvents enabling them to be formulated, for example, as spin coated films. The Q-band absorptions in these 3:1 macrocycles containing an annellated π electron deficient heterocycle are shifted to the blue relative to the Q-band of series **1**, in line with general predictions from MO calculations undertaken

---

Keywords: phthalocyanines; macrocycles; thiophenes; liquid crystals.

* Corresponding author. Fax: +44-1603-592015;
e-mail: m.cook@uea. ac.uk

0040–4020/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(00)00323-9

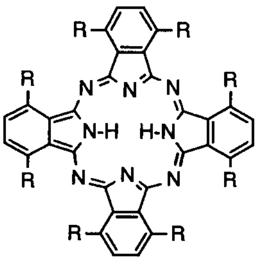


3 R = C_8H_{17}, R' = R" = H
4 R = C_8H_{17}, R' = R" = CH_3
5 R = R' = R" = C_8H_{17}
6 R = C_8H_{17}, R' = CH_3, R" = $C_6H_{12}OH$
7 R = C_6H_{13}, R' = R" = H
8 R = C_6H_{13}, R' = R" = CH_3

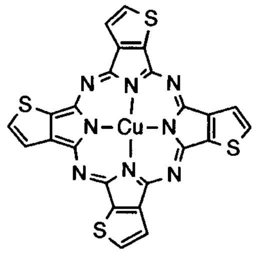
6a R = C_8H_{17}, R' = CH_3, R" = $C_6H_{12}OH$, M = Ni
7a R = C_6H_{13}, R' = R" = H, M = Ni
7b R = C_6H_{13}, R' = R" = H, M = Co
7c R = C_6H_{13}, R' = R" = H, M = Zn
7d R = C_6H_{13}, R' = R" = H, M = Cu

Scheme 1. Cross tetramerisation route to tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine derivatives.

within the framework of the PPP approximation.[12]



1 R = alkyl



2

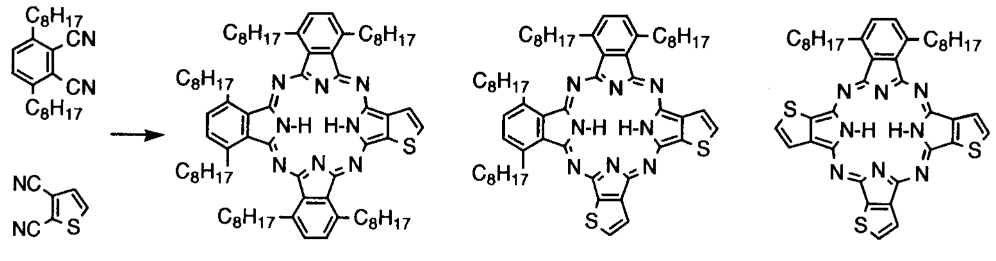
The present paper focuses on novel macrocyclic systems derived from incorporation of the π electron rich thiophene ring in place of the benzenoid rings of phthalocyanine. Hitherto, Linstead and coworkers[13] prepared tetrathiopheno[2,3]porphyrazine during the original studies of phthalocyanines in the 1930s. They reported the synthesis of the copper(II) derivative, presumably as an isomeric mixture of which structure **2**, M=Cu, is an example, describing the product as being greener than phthalocyanine itself.[13] More recently, Knawby and Swager described some octa-alkoxymethyl analogues of the series.[14] Here we describe compounds in which thiophene replaces one,[15] two or three of the four benzenoid rings of structure **1**. Compounds have been obtained by cross cyclotetramerisation reactions of 3,6-dialkylphthalonitriles with 3,4-dicyanothiophene, some 2,5-dialkyl-3,4-dicyanothiophenes, and 2,3-dicyanothiophene. Tetrathiophenoporphyrazines obtained from reaction of a 2,5-dialkyl-3,4-dicyanothiophene with 2,3-dicyanothiophene are also investigated.

Results and Discussion

Cross reactions between 3,6-dialkylphthalonitriles and 3,4-dicyanothiophenes

The route to 3,6-dialkylphthalonitriles has been described in earlier papers from these laboratories.[16,17] 3,4-Dicyanothiophene[18] was prepared from commercially available 3,4-dibromothiophene by the Rosenmund von Braun reaction with copper(I) cyanide. 2,5-Dialkyl-3,4-dicyanothiophenes were prepared from thiophene via ring dialkylation at the 2,5-positions,[16] dibromination at the 3,4 positions and a Rosenmund von Braun reaction to introduce the cyano groups.

In earlier work from these laboratories 3:1 Pcs have been routinely prepared by lithium pentyloxide catalysed reaction of two phthalonitrile precursors in the ratio of 9:1, giving a fully symmetrical Pc derived from the major component and the required 3:1 Pc.[16,17] Use of the 9:1 ratio minimises the formation of other cross tetramerisation products so facilitating isolation of the 3:1 product. In this work, preliminary studies of reactions between 3,6-dialkylphthalonitriles and 2,5-dialkyl-3,4-dicyanothiophenes indicated that the 9:1 ratio produced little, if any, thiophene containing macrocycle, indicating the lower reactivity of 3,4-dicyanothiophenes compared to phthalonitriles. However, a ratio of 4:1 produced small amounts of thiopheno[3,4]tribenzoporphyrazines, isolated as the metal-free derivatives, **3**–**8**, alongside the corresponding symmetrically substituted octaalkylphthalocyanine, **1**, Scheme 1. Recovered yields of the former generally depended upon the ease of the chromatographic separation; the hexa-alkylated derivatives **3** and **7** were recovered in yields of 12 and 11%, respectively; yields for compounds **4**, **6** and **8** were lower at 7, 6 and 5%, respectively. Unsurprisingly, the octaoctyl derivative **5** was particularly difficult to separate from octaoctylphthalocyanine and a pure sample was obtained in just 1% yield. Examples of metallated derivatives, **6a** and **7a**–**d**, were prepared from the corresponding metal-free macrocycles by reaction with the appropriate metal(II) acetate in pentanol solution heated to reflux. All compounds gave satisfactory C, H and N data. Metal-free



9 **10** **11**

Scheme 2. Products of a cross tetramerisation of 3,4-dioctylphthalonitrile and 2,3-dicyanothiophene. Octaoctylphthalocyanine, not shown, is also formed.

and compounds metallated with diamagnetic ions gave ^{1}H NMR spectra consistent with the assigned structure. Satisfactory FAB-MS were obtained for the metallated derivatives but metal-free compounds were prone to fragmentation.

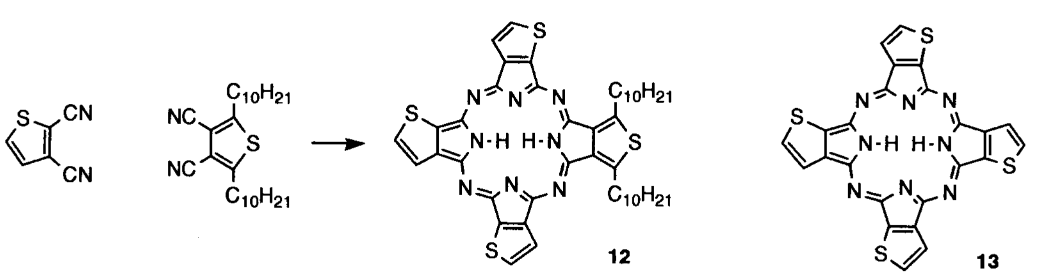
Cross reactions between 3,6-dialkylphthalonitriles and 2,3-dicyanothiophene

2,3-Dicyanothiophene[18] was prepared from 2,3-dibromothiophene (commercially available) using CuCN under essentially the same conditions used to prepare the 3,4-dicyanothiophene series. Unlike the reactions leading to the latter, the product was contaminated with amounts of green/blue impurity, λ_{max} (THF): 353, 585 and 646 nm, presumed to be the copper(II) complex **2**. The reactivity of 2,3-dicyanothiophene in cross reactions with 3,6-dialkylphthalonitriles is higher than that of 3,4-dicyanothiophene. Thus the cross tetramerisation of 3,6-dioctylphthalonitrile and 2,3-dicyanothiophene, Scheme 2, in a 9:1 ratio afforded a complex mixture. This was separated by column chromatography. The first and second fractions were the expected octaoctylphthalocyanine **1** and the 3:1 product, the thiopheno[2,3]tribenzoporphyrazine, **9** (7% yield). Two further fractions were shown by elemental analysis, ^{1}H NMR spectroscopy and low resolution FAB-MS to be the 2:2 (2%) and 1:3 crossed products (1%), viz dibenzodithiopheno[2,3]porphyrazines and benzotrithiopheno[2,3]-porphyrazines, respectively. These are expected to be formed as regioisomeric mixtures, of which a single example for each, **10** and **11**, is shown in Scheme 2. Isomerism arises from the different possible orientations of the thiophene rings with respect to each other. It is possible that isomers of **10** in which the heterocyclic rings are opposite each other are present though statistical considerations regarding stepwise cyclisations suggest these are less likely.

^{1}H NMR data are unhelpful in unravelling the content of the isomer mixtures because of overlapping signals. On traversing the series **9**, **10** and **11**, the chemical shifts of the N–H protons at the centre of the macrocycles are shifted upfield.

Cross reactions between 3,4-dicyano-2,5-didecylthiophene and 2,3-dicyanothiophene

Reaction of 3,4-dicyano-2,5-didecylthiophene and 2,3-dicyanothiophene (ratio 7:1) under the standard conditions gave a blue product mixture dominated by a slow moving fraction on TLC. Column chromatographic separation of the two smaller preceding fractions afforded first a fraction whose mass spectrum showed the presence of 3:1 and 2:2 crossed condensed compounds, i.e. containing respectively three and two components derived from 3,4-dicyano-2,5-didecylthiophene [FAB-MS (LSIMS): 1380 and 1099]. This mixture was formed in ca. 1% yield and was not separated further. The UV–vis spectrum of a solution in THF showed some substantially red shifted bands, λ_{max} 326, 615, 675, 779 and 820 nm. The second fraction from the column, obtained by elution with warm THF, corresponded to an isomer mixture of the 1:3 macrocycles, i.e. compounds derived from one part 3,4-dicyano-2,5-didecylthiophene and three parts 2,3-dicyanothiophene, e.g. **12**, [FAB-MS (LSIMS): 818]. The presence of regioisomers was deduced from the ^{1}H NMR spectrum. For example there is a group of singlets for the protons in the centre of the macrocycles located at ca. −3 ppm and integrating in total for two protons. The mixture shows λ_{max} 342, 631, 664, with the main Q-bands at 701 and 740 nm. The third and major fraction, slow moving but elutable with hot THF, was assigned to self condensation products of 2,3-dicyanothiophene, e.g. **13**, λ_{max} 351, 574, 617, 632, 676 nm. The ready formation of products derived from 2,3-dicyanothiophene, despite it



12 **13**

Scheme 3. Principal products recovered from the cross cyclotetramerisation reaction between 2,3-dicyanothiophene and 2,5-didecyl-3,4-dicyanothiophene, the latter in excess.

Table 1. UV–Visible spectroscopic data of solutions (in cyclohexane) and spin coated film

Compound	Solution phase λ_{max}/nm ($\epsilon/10^5$)	Spin coated films λ_{max}/nm (Relative intensities)
3	333 (0.78), 663 (1.15), 687 (0.63), 705 (0.71), 742 (2.40)	332 (1.0), 657 (0.68), 795 (0.87)
4	306 (0.92), 336 (1.01), 674 (1.11), 706 (0.87), 727 (0.79),764 (2.01)	337 (1.0), 630 (0.60), 704 (0.82),783 (0.76)
5	307 (0.69), 337 (0.75), 677 (0.79), 708 (0.68), 729 (0.63), 768 (1.39)	341 (1.0), 657 (0.61), 817 (0.55)
6	309 (0.53), 340 (0.61), 678 (0.76), 709 (0.60), 731 (0.54), 768 (1.39)	337 (1.0), 654 (0.81), 689 (0.78),782 (0.59)
6a	300 (0.73), 337 (0.49), 622 (0.30), 675 (0.63), 693 (0.89), 738 (1.24)	338 (0.85), 638 (0.92), 675 (1.0), 750 (0.66)
7	336 (0.56), 386 (0.36), 662 (0.88), 687 (0.48), 705 (0.54), 742 (1.81)	332 (1.0), 370 (0.92), 653 (0.70),795 (0.98)
7a	298 (1.10), 333 (0.67), 614 (0.43), 681 (1.89), 716 (2.35)	335 (0.85), 660 (0.77), 765 (1.0)
7b	283, 678, 714[a]	322 (1.0), 673 (0.72), 769 (0.89)
7c	336 (0.67), 689 (1.25), 726 (1.38)	339 (1.0), 654 (0.74), 802 (0.67)
7d	335 (0.71), 686 (1.04), 722 (1.14)	337 (1.0), 647 (0.79), 787 (0.83)
8	336 (0.69), 674 (0.87), 705 (0.67), 726 (0.61), 764 (1.57)	338 (1.0), 641 (0.87), 705 (0.89), 736 (0.83), 778 (0.73)
9	347 (0.79), 648 (1.11), 679 (0.80), 700 (0.85), 720 (1.64)	334 (1.0), 624 (0.68), 784 (0.64)
10	344 (0.62), 593 (0.30), 634 (0.54), 654 (1.00), 695 (1.65)	344 (1.0), 628 (0.66), 744 (0.77)
11	345 (0.97), 619 (1.08), 645 (0.81), 673 (0.89), 697 (1.43)	345 (1.0), 614 (0.62), 705 (0.49), 778 (0.49)
12	342, 631, 664, 701, 740[b]	353 (1.0), 610 (0.56), 691 (0.63), 772 (0.47)

[a] Sample decomposes during running of spectrum.

[b] Insufficient sample to measure ϵ.

being the minor component of the reaction mixture, confirms its greater reactivity over that of the dialkyl 3,4-dicyanothiophenes (Scheme 3).

The availability of 3,4-dicyanothiophenes in this work enabled us to test Linstead's original hypothesis[13] that self condensation of 3,4-dicyanothiophene should not produce tetrathiopheno[3,4]porphyrazine because an aromatic structure for this compound can only be drawn with the involvement of unconventional resonance canonicals. Recently, however, there has been a report that Schiff base derivatives of 2,5-diamino-3,4-dicyanothiophene are converted into the corresponding tetrathiopheno[3,4]porphyrazines, though no details of the characterisation of the products were given.[19] In our hands, attempted self condensations of examples of the present 3,4-dialkylthiophenes gave dark brown reaction mixtures, a bad odour, and no visible region absorption which would be characteristic of a phthalocyanine-type macrocycle.

UV–Visible spectroscopy

For D_{4h} symmetrical phthalocyanines metallated at the centre, e.g. with M(II) ions, the Q-band absorption is assigned to transitions $a_{1u} \rightarrow e_g$ leading to a doubly degenerate state, ^1E_u, which is observed as a single intense absorption at ca. 700 nm. The lower symmetry of metal-free phthalocyanines, e.g. **1**, leads to a more complex set of orbitals in which the two lowest energy unoccupied orbitals are no longer degenerate. Thus the Q-band is split into two components. The compounds investigated in this study, both metallated and metal-free, are also of lower symmetry than D_{4h} with a π system perturbed by the presence of one or more π electron rich thiophene rings. Spectroscopic data for these compounds as solutions in cyclohexane (ca. 10^{-6} M) are collected in Table 1 and examples of spectra appear as Fig. 1.

The metallated compounds give rise to (apparently) simpler Q-band absorptions than the metal-free derivatives. Each shows two main components with low intensity bands to the blue which are expected to be vibronic in origin. Comparison of Q-band data for the two nickel containing derivatives, **6a**, λ_{max} 693 and 738 nm, and **7a**, λ_{max} 681 and 716 nm, shows that the Q-band absorption is particularly sensitive to the presence of substituents on the thiophene ring; those in the former give rise to a bathochromic shift and an increase in the splitting. Alkyl groups in the non-peripheral (or α) locations on the phthalocyanine ring, as in series **1**, are also known to cause a bathochromic shift. A nickel(II) octaalkylphthalocyanine shows λ_{max} 705 nm.[20] However, this is well to the blue of the lowest energy Q-band component of **6a**. Data for series **7a**–**7d** indicate that the metal ion has some small influence on the energy of the absorption and the trend generally follows that found in metallated Pcs.[20]

The spectra for metal-free derivatives **3**–**7** are characterised by four strong bands in the visible region, together with lower intensity vibronic bands to the blue, Table 1 and see Fig. 1. Of the four, the lowest and highest energy bands have the strongest absorbance and these we assign to the two components of the Q-band. For compounds **3** and **7**, which are not substituted on the thiophene ring, the bands appear at 662–663 and 742 nm. Those bearing methyl substituents, **4** and **8**, show λ_{max} 674 and 764 nm; those with longer chains, **5** and **6**, show λ_{max} 677–678 and 768 nm. The two lower intensity bands intermediate between the Q-band components we assign to the 0→1 and 0→2 vibronic transitions of the lower energy Q-band absorption; their intensities, compared to the low intensity bands in phthalocyanines, imply a high distortion of the molecular geometry on excitation. The data for the octaalkyl substituted macrocycles **5** and **6**, λ_{max} 677–678 and 768 nm, are best compared with Q-band data for octaalkylphthalocyanines of series **1**, λ_{max} 694 and 728 nm. There is evidently a much greater splitting in the spectra of **5** and **6** and a red shift of the lower energy component.

The spectrum of **9**, Fig. 1, where the thiophene ring is fused at the 2,3-bond, shows similar features with λ_{max} 648 and 720 nm for the two Q-band components. These are thus blue shifted relative to the corresponding absorptions in the isomeric 3,4-fused compound **3**. Compounds **10** and **11** were each obtained as isomeric mixtures, which show a blue shift of the lowest energy band relative to **9**.

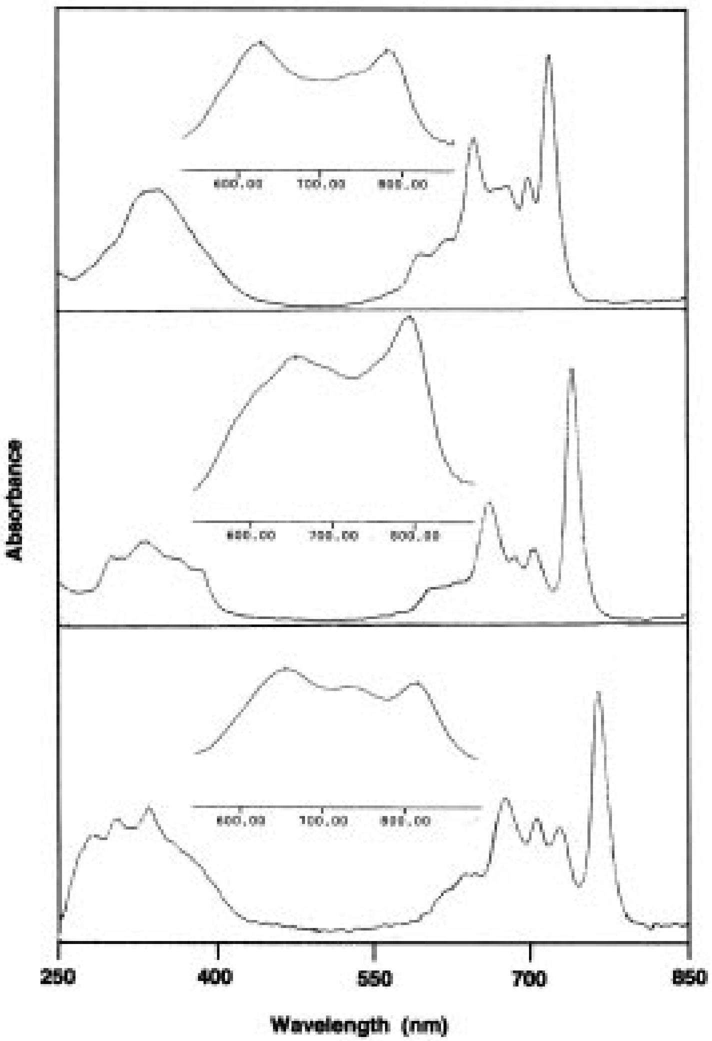


Figure 1. UV–Visible absorption spectra of solutions in cyclohexane and, inset, the visible region spectra of spin coated films of: top, 7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[2,3-q]porphyrazine **9**; middle, the isomeric 7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine **3**; bottom, 1,3,7,10,14,17,21,24-octaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine **5**.

Spin coated films and solid state spectra

The large splitting of the Q-band absorption described above extends the absorption envelope over a broad band of wavelengths. Broad band absorbers have potential as filters and as light absorbing molecules for devices such as non silicon based solar cells. Such applications would use compounds in the solid state. The solid state spectra were recorded of the compounds formulated as spin coated films on glass slides. The films were prepared by administering a drop of a solution of known concentration of the compound in THF onto the slide rotating at 2000 rpm. After ca. 20 seconds the solvent had evaporated to give an even film as judged by ellipsometry, thickness ca. 1000 Å. There was no evidence of crystallites on inspection through a microscope. Visible region absorptions, reported in Table 2 with examples shown as insets in Fig. 1, show band envelopes which are much broader than those observed earlier for films of series **1** and their metallated derivatives.[21] In some instances they extend from the red into the near infra-red, some beyond 800 nm.

Liquid crystal behaviour

The melting properties of the compounds were investigated using polarised light microscopy and, for some examples, differential scanning calorimetry (DSC). Those compounds bearing six alkyl chains or more exhibited thermotropic liquid crystal behaviour giving rise to columnar mesophases comparable to those exhibited by examples of series **1** and their metallated analogues, as well as related phthalocyanines.[11,22] Transition temperatures and enthalpic data are collected in Table 2. Mesophases are formed on both heating and cooling cycles. The birefringence textures were best investigated during cooling; in each case a fan type texture was observed upon cooling the compound from the isotropic liquid (I). The texture is characteristic of a columnar phase denoted as D_{hd}, with hexagonal cross sectional symmetry, and with disorder within the column. Some compounds entered a lower temperature mesophase on further cooling, showing a characteristic needle-like texture. Previous work indicates that this may be a rectangular disordered columnar mesophase, D_{rd}.[22]

Table 2. Transition temperatures and enthalpy data (transition temperatures measured by polarised light microscopy and confirmed by DSC. ΔH Values measured by DSC (rate 10°C/min) on the cooling cycle and second heating cycle. (–) Indicates enthalpy change is too low to be measured) for mesophase transitions (K represents the highest temperature crystal state for each particular derivative. The higher temperature mesophase is assigned as D_{hd}. The lower temperature mesophase is tentatively assigned as D_{rd} (see text))

Compound		Transition temperatures (°C), ΔH (kJmol^{-1})							
		$K\rightarrow D_{hd}$	$K\rightarrow D_{rd}$	$D_{rd}\rightarrow D_{hd}$	$D_{hd}\rightarrow I$	$I\rightarrow D_{hd}$	$D_{hd}\rightarrow D_{rd}$	$D_{rd}\rightarrow K$	$D_{hd}\rightarrow K$
3	T	164			212	209			142
	ΔH	61.4			7.8	7.1			59.9
4	T		79	170	233	230	168	47	
	ΔH		41.6	–	–	–	–	45.6	
5	T		80	133	212	207	127	52	
	ΔH		47.0	–	–	–	–	46.8	
6	T		53	125	208	201	123	44	
6a	T	91			235	231			85
	ΔH	[a]			8.3	9.0			[a]
7	T	158			231	229			145
	ΔH	51.5			4.6	4.4			46.3
7a	T		151	248	267	265	245	137	
7b	T		144	278	302	301	272	119	
7c	T		170	298	337	334	298	155	
7d	T		166	269	307	300	261	156	
8	T		125	225	248	246	223	102	
	ΔH		52.9	–	7.4	7.8	–	50.5	
9	T	171			212	208			146
	ΔH	59.6			6.2	6.6			59.0

[a] Not measured.

Data in Table 2 reveal that trends observed for series **1** and its metallated derivatives[11] are followed by series in the present work. Thus where comparisons allow, increase of the length of chains attached to the benzenoid rings lowers the crystal to mesophase transition temperature and increases the temperature range over which the mesophases exist. However, the presence of the thiophene unit also stabilises the mesophase. Compound **5** with eight octyl chains has a mesophase range which is about 65°C greater than that observed for octaoctylphthalocyanine, **1** R=octyl. This increase in mesophase stability arises largely from a higher mesophase to isotropic liquid (D→I) transition temperature of the thiophene analogue. We attribute this to enhanced intermolecular dipolar interactions brought about by the presence of the strong lateral dipole within the structure of thiophene based systems.[23] Somewhat unexpectedly, the mesophase range exhibited by compound **4**, six octyl groups and two methyl groups, is wider than that exhibited by compound **5**. Comparison of the phase transitions for the isomeric compounds **3** and **9** shows that the two have similar mesophase ranges and the same transition temperature from the mesophase to the isotropic liquid.

Conclusion

Cross cyclotetramerisation reactions between a 3,6-dialkylphthalonitrile, a 3,4-dicyanothiophene and 2,3-dicyanothiophene have been undertaken to obtain novel 3:1 cross products, *ie* macrocycles related to phthalocyanine in which one (or more) of the benzenoid rings of the latter are replaced by thiophene rings. Product analysis of reactions indicate that 2,3-dicyanothiophene is the most reactive and 3,4-dicyanothiophene is the least reactive in these cross reactions. Tribenzothiopheno[3,4]porphyrazines, 3:1 macrocycles obtained from condensations of 3,6-dialkylphthalonitriles and 3,4-dicyanothiophene or 2,5-dialkyl-3,4-dicyanothiophenes, show a strongly split Q-band absorption, one component of which is highly red shifted relative to the corresponding band in an octa-alkylphthalocyanine. The degree of splitting and the extent of the red shift is dependent upon whether or not the macrocycle is metallated and the total number of alkyl substituents on the ring. The compounds form even, transparent spin-coated films which exhibit a broad band absorption envelope in the far red/near infra red region of the spectrum. Hexaoctyl tribenzothiopheno[2,3]porphyrazine shows similar distortion of the Q-band absorption but to a lesser degree than the isomeric hexaoctyl tribenzothiopheno[3,4]porphyrazine. These compounds, metallated or unmetallated, exhibit columnar mesophase behaviour. Where a comparison allows, mesophase stability, assessed by the temperature range over which the mesophases exist, is greater for an octa-alkylated tribenzothiopheno[3,4]porphyrazine than for the corresponding alkyl substituted phthalocyanine. Reaction of 2,3-dicyanothiophene with a 2,5-dialkyl-3,4-dicyanothiophene, the latter in excess, gives a product mixture rich in macrocycles derived predominantly from the former.

Experimental

IR spectra were recorded on a Perkin–Elmer 297, 298 or a FTIR 1720 spectrophotometer as either neat liquids or as nujol mulls of solids. ^{1}H NMR spectra were measured at 60 MHz using a JEOL JNM-PMX 60 spectrometer and at 270 MHz using a JEOL EX 270 spectrometer. Routine mass spectra were recorded using a Kratos model MS25 magnetic sector mass spectrometer using electron impact ionisation. FAB-MS (LSIMS) were obtained using nitrobenzyl alcohol as the matrix and were measured using the EPSRC's VG ZAB-E low resolution equipment at Swansea University. UV–Vis spectra of solutions and films were measured using a Hitachi U-3000 spectrophotometer. Melting points were measured and thermotropic mesophase behaviour determined using an Olympus BH-2 polarising microscope in conjunction with a Linkam TMS 92 thermal analyser and a Linkam THM 600 cell. Differential scanning calorimetry (DSC) of each compound (3–5 mg) was undertaken using a Thermal Analyst 2000 in conjunction with a DSC 10 Differential Scanning Calorimeter from TA Instruments at a heating and cooling rate of 10°C min^{-1}. Spin-coated (SC) films were formulated by administering a drop of a solution of a compound in THF (ca. 2 mg in 0.5 ml) onto a glass slide (BDH Cat. No. 406/0180/02; size 76×26 mm^2, 0.8–1.0 mm thick) rotating at 2000 rpm for a period of 20 seconds on a Headway Spinner.

Silica gel (Merck 7734) was used in chromatographic separations. TLC was performed using silica gel (Merck 5554) supported on aluminium sheets. Solvents were dried, where appropriate, over sodium and distilled under an atmosphere of dry nitrogen.

2-Methylthiophene, 2,5-dimethylthiophene and 3,4-dibromothiophene were purchased from Sigma–Aldrich Ltd. 2,5-Dioctylthiophene, 2,5-didecylthiophene, 3,6-dihexylphthalonitrile, 3,6-dioctylphthalonitrile and 2-(6-iodohexyloxy)tetrahydropyran were prepared by routes previously reported from these laboratories.[16,17,22] 2,3-Dicyanothiophene (mp 123.6°C, lit.[18] mp 150°C). *m*/*z* 134. (Found: C, 53.87; H, 1.39; N, 20.79. $C_6H_2N_2S$ requires: C, 53.72; H, 1.50; N, 20.88%) and 3,4-dicyanothiophene (mp 174°C, lit.[18] mp 171°C). *m*/*z* 134. (Found: C, 53.84; H, 1.38; N, 21.09; S, 23.92. $C_6H_2N_2S$ requires: C, 53.72; H, 1.50; N, 20.88; S, 23.90%) were prepared by literature procedures.[18]

2-Methyl-5-[6-(2-tetrahydropyranyloxy)hexyl]thiophene. 1.14 equiv. of *n*-BuLi (32 ml of 2.5 M solution in hexane, 80 mmol) were added via a cannula to a stirred solution of 2-methylthiophene (6.86 g, 70 mmol) in dry THF (50 ml) under an atmosphere of dry argon at −78°C. The mixture was allowed to warm to rt and stirred for 3 h. The mixture was cooled to −78°C and 2-(6-iodohexyloxy)tetrahydropyran (24 g, 77 mmol) was added dropwise. The mixture was allowed to warm to rt and left to stir for a further 16 h. The reaction mixture was then poured onto ice (300 g) and the crude product extracted with diethyl ether (2×150 ml). The organic solution was washed with saturated brine (200 ml), dried ($MgSO_4$), filtered and the solvents removed under reduced pressure to yield *2-methyl-5-[6-(2-tetrahydropyranyloxy)hexyl]thiophene* as a pale yellow oil (16.8 g, 85%), *m*/*z* 282, which was used without further purification. δH (60 MHz; $CDCl_3$): 1.2–2.0 (m, 14H), 2.4 (s, 3H), 2.72 (t, J=7.0 Hz, 2H), 3.2–4.0 (m, 4H), 4.56 (br s, 1H), 6.54 (s, 2H).

3,4-Dibromo-2,5-dioctylthiophene. In a typical procedure, bromine (12.4 g, 155 mmol) was added slowly to a stirred solution of 2,5-dioctylthiophene (11.97 g, 39 mmol) in glacial acetic acid (100 ml) at −5°C over 1 h and the solution was allowed to warm to rt over 18 h. The acetic acid was removed under reduced pressure and the residue was poured onto ice (200 ml) and extracted with diethyl ether (2×100 ml) and DCM (2×100 ml). The organic extracts were combined and washed with saturated brine (200 ml), dried ($MgSO_4$), filtered and evaporated under reduced pressure to afford crude *3,4-dibromo-2,5-dioctylthiophene* (14.5 g, 80%) as a red–orange oil, *m*/*z* 466, which was used without further purification. δH (60 MHz; $CDCl_3$): 0.9 (t, J=6.6 Hz, 6H), 1.08–1.84 (m, 24H), 2.8 (t, J=7.2 Hz, 4H).

3,4-Dibromo-2,5-didecylthiophene. Prepared as above from 2,5-didecylthiophene. The *compound* was obtained as a red oil (yield of 65%); *m*/*z* 522. δH (60 MHz; $CDCl_3$): 0.9 (t, J=7.8 Hz, 6H), 1.3 (br s, 32H), 2.8 (br t, 4H) and used without further purification.

3,4-Dibromo-2,5-dimethylthiophene. Prepared as above from 2,5-dimethylthiophene. The *compound* was recrystallised from DCM-light petroleum and isolated as light brown crystals (mp. 45°C, 75%); *m*/*z* 270. (Found: C, 26.76; H, 2.09; S, 11.7; Br, 58.62. $C_6H_6Br_2S$ requires: C, 26.69; H, 2.24; S, 11.87; Br, 59.19%). δH (60 MHz; $CDCl_3$): 2.4 (s, 2H).

3,4-Dibromo-2-(6-hydroxyhexyl)-5-methylthiophene. Prepared as above from 2-methyl-5-[6-(2-tetrahydropyranyloxy)hexyl]thiophene. The compound was obtained as a pale brown–red oil (40%), and used without further purification. δH (60 MHz; $CDCl_3$): 1.1–2.0 (m, 8H), 2.40 (s, 3H), 2.70 (t, J=7.0 Hz, 2H), 3.52 (t, J=6.0 Hz, 2H).

3,4-Dicyano-2,5-dioctylthiophene. 3.2 equiv. of CuCN (5 g, 56 mmol) were added to a stirred solution of 3,4-dibromo-2,5-dioctylthiophene (8.25 g, 17.7 mmol) in dry DMF (25 ml). The mixture was refluxed under an atmosphere of dry nitrogen for about 6 h. The mixture was allowed to cool, poured onto a stirred solution of $FeCl_3$ (20 g in 100 ml 2 M HCl (aq)) and heated to 60–70°C for 30 min. After cooling, the solution was extracted with DCM (4×120 ml) and the extract washed with 2 M HCl (aq) (300 ml), water (400 ml), saturated solution of $NaHCO_3$ (aq) (300 ml), and water (400 ml). The solution was dried ($MgSO_4$), filtered and solvents removed under reduced pressure to afford crude 3,4-dicyano-2,5-dioctylthiophene (3.2 g, 50%) as an orange oil which solidified on standing for a week. Recrystallisation from ethanol afforded *3,4-dicyano-2,5-dioctylthiophene* as a colourless solid mp 30.1°C; *m*/*z* 358. (Found: C, 73.93; H, 9.54; N, 7.81. $C_{22}H_{34}N_2S$ requires: C, 73.69; H, 9.56; N, 7.81%). ν_{max} (nujol)/cm^{-1}: 2222 (CN); δH (60 MHz; $CDCl_3$): 0.88 (t, J=6.8 Hz, 6H), 1.30 (br s, 24H), 2.96 (t, J=7.2 Hz, 4H).

3,4-Dicyano-2,5-didecylthiophene. Prepared as above from 3,4-dibromo-2,5-didecylthiophene. The *compound* was obtained as a colourless solid (mp 40.1°C, 56%). *m*/*z* 414. (Found: C, 75.40; H, 10.24; N, 6.45. $C_{26}H_{42}N_2S$ requires: C, 75.31; H, 10.21; N, 6.76%). ν_{max} (nujol)/cm^{-1}: 2222 (CN).

3,4-Dicyano-2,5-dimethylthiophene. Prepared as above from 3,4-dibromo-2,5-dimethylthiophene. The *compound* was obtained as a colourless solid (mp 214.8°C, 65%); *m*/*z* 162. (Found: C, 59.41; H, 3.55; N, 17.19; S, 19.83. $C_8H_6N_2S$ requires: C, 59.24; H, 3.73; N, 17.27; S, 19.76%). ν_{max} (nujol)/cm^{-1}: 2220 (CN); δH (60 MHz; $CDCl_3$): 2.62 (s, 6H).

3,4-Dicyano-2-(6-hydroxyhexyl)-5-methylthiophene. Prepared as above from 3,4-dibromo-2-(6-hydroxyhexyl)-5-methylthiophene. The *compound* was obtained as a pale yellow solid (mp 39°C, 40%); *m/z* 248. (Found: C, 62.73; H, 6.56; N, 10.82; S, 12.65. $C_{13}H_{16}N_2OS$ requires: C, 62.87; H, 6.49; N, 11.28; S, 12.91%). ν_{max} (nujol)/cm^{-1}: 3400 (OH), 2220 (CN). δH (60 MHz; CDCl$_3$): 1.1–2.0 (m, 8H), 2.16 (s, 1H), 2.64 (s, 3H), 2.96 (t, *J*=7.1 Hz, 2H), 3.68 (t, *J*=6.0 Hz, 2H).

Crossed cyclic tetramerisation reactions of 3,6-dialkylphthalonitriles and 3,4-dicyanothiophenes. Synthesis of alkyl substituted 28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazines, (3–8)

In a typical procedure, 3,6-dioctylphthalonitrile (3.28 g, 9.3 mmol) and 3,4-dicyanothiophene (0.3 g, 2.2 mmol) in dry pentan-1-ol (30 ml) were heated under reflux with stirring. Lithium metal (0.2 g) was added slowly in small portions. The solution which turned an intense green colour immediately was heated to reflux for 6 h. The mixture was allowed to cool to rt and glacial acetic acid (50 ml) was added. Stirring was continued for 30 min. The solvents were removed under reduced pressure and the mixture washed onto a filter with methanol (500 ml). Washing with THF dissolved the desired products leaving a residue of salts and non-macrocyclic products. The THF was removed under reduced pressure and the mixture separated by chromatography (silica). The first green fraction, eluted with light petrol, was metal-free 1,4,8,11,15,18,22,25-octaoctylphthalocyanine. The second green fraction, eluent THF, was purified by further column chromatography, eluent light petroleum–DCM (7:1), and recrystallised from THF–methanol to obtain *7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 3:* as a blue solid (290 mg, 11% based on 3,4-dicyanothiophene), mp 164°C (K→D), 212°C (D→I). (Found: C, 78.48; H, 9.55; N, 9.26; S, 2.72. $C_{78}H_{112}N_8S$ requires: C, 78.47; H, 9.46; N, 9.39; S, 2.69%). δH (270 MHz; C_6D_6; 50°C): −0.58 (s, 2H), 0.80–0.95 (m, 18H), 1.2–2.0 (m, 60H), 2.28–2.45 (m, 12H), 4.34 (t, *J*=6.8 Hz, 4H), 4.62–4.72 (m, 8H), 7.81 (d, *J*=7.6 Hz, 2H), 7.87 (s, 2H), 7.88 (d, *J*=7.6 Hz, 2H), 8.28 (s, 2H); λ_{max} (cyclohexane)/nm: 333, 663, 687, 705, 742.

The following were prepared similarly from the appropriate dicyanothiophene and dialkylphthalonitrile.

1,3-Dimethyl-7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 4. Following reaction of 3,6-dioctylphthalonitrile (3.57 g) and 3,4-dicyano-2,5-dimethylthiophene (0.5 g), the first fraction from column chromatography (silica: eluent petrol) removed metal-free 1,4,8,11,15,18,22,25-octaoctylphthalocyanine. Subsequent fractions were combined and rechromatographed with graded elution commencing with petrol, 5% added DCM, and 10% added DCM. Compound **4** was obtained as a blue crystalline solid, (0.19 g, 7% based on 3,4-dicyano-2,5-dimethylthiophene), mp 79°C (K→D), 233°C (D→I). (Found: C, 79.03; H, 9.27; N, 8.98. $C_{80}H_{116}N_8S$ requires: C, 78.64; H, 9.57; N, 9.17%). δH (270 MHz; C_6D_6 50°C): −0.72 (s, 2H), 0.81–0.91 (m, 18H), 1.2–2.0 (m, 64H), 2.31 (m, 4H), 2.44 (m, 4H), 2.66 (s, 6H), 3.74 (t, *J*=7.4 Hz, 4H), 4.55 (t, *J*=7.0 Hz, 4H), 4.69 (t, *J*=7.2 Hz, 4H), 7.58 (d, *J*=7.6 Hz, 2H), 7.74 (d, *J*=7.6 Hz, 2H), 7.93 (s, 2H); λ_{max} (cyclohexane)/nm: 306, 336, 674, 706, 727, 764.

1,3,7,10,14,17,21,24-Octaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 5. The compound was obtained as the first column fraction (eluent: light petroleum) from reaction of 3,6-dioctylphthalonitrile (1.82 g) and 3,4-dicyano-2,5-dioctylthiophene (0.3 g). Recrystallisation from THF–methanol afforded the product **5** as a blue solid (10 mg, 1% based on 3,4-dicyano-2,5-dioctylthiophene), mp 80°C (K→D), 212°C (D→I). (Found: C, 79.59; H, 10.37; N, 7.75. $C_{94}H_{144}N_8S$ requires: C, 79.61; H, 10.23; N, 7.90%). δH (270 MHz; C_6D_6): −0.17 (s, 2H), 0.87 (t, 24H), 1.2–1.9 (m, 80H), 2.11 (t, 4H), 2.2–2.4 (m, 12H), 3.82 (t, *J*=7.1 Hz, 4H), 4.27 (t, *J*=6.8 Hz, 4H), 4.56–4.67 (m, 8H), 7.7–7.84 (m, 6H); λ_{max} (cyclohexane)/nm: 307, 337, 677, 708, 729, 768.

1-(6-Hydroxyhexyl)-3-methyl-7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine (6). The first separation (silica: petrol) of products from reaction of 3,6-dioctylphthalonitrile (3.58 g) and 3,4-dicyano-2-(6-hydroxyhexyl)-5-methylthiophene (0.41 g) afforded metal-free 1,4,8,11,15,18,22,25-octaoctylphthalocyanine as the first fraction. Subsequent fractions were combined and re-chromatographed [silica: petrol–THF (4:1)] to afford compound **6** as blue crystals, [135 mg, 6% based on 3,4-dicyano-2-(6-hydroxyhexyl)-5-methylthiophene], mp 208°C (D→I). (Found: C, 78.10; H, 9.97; N, 8.34. $C_{85}H_{126}N_8OS$ requires: C, 78.05; H, 9.71; N, 8.57%). δH (270 MHz; C_6D_6): −0.87 (s, 2H), 0.92 (br t, 18H), 1.2–2.5 (m, 81H), 2.60 (s, 3H), 3.27 (t, *J*=6.0 Hz, 2H), 3.41 (t, *J*=6.0 Hz, 4H), 3.87 (t, *J*=5.8 Hz, 2H), 4.27 (br t, 2H), 4.5–4.6 (m, 4H), 4.66 (br t, 2H), 7.28 (d, *J*=7.8 Hz, 1H), 7.49 (d, *J*=7.8 Hz, 1H), 7.63 (d, *J*=7.6 Hz, 1H), 7.77 (d, *J*=7.6 Hz, 1H), 7.87 (s, 2H); λ_{max} (cyclohexane)/nm: 309, 340, 678, 709, 731, 768.

7,10,14,17,21,24-Hexahexyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 7. Chromatography (silica: eluent light petrol) of products from reaction of 3,6-dihexylphthalonitrile (2.5 g) and 3,4-dicyanothiophene (0.4 g) afforded octahexylphthalocyanine **1**, R=C_6H_{13} as the first fraction. Change of eluent to cyclohexane–DCM (10:1) provided a second fraction which was re-chromatographed, silica: petrol–THF (4:1) to afford compound **7** as a blue crystalline solid, (0.31 g, 11% based on 3,4-dicyanothiophene), mp 158°C (K→D), 231°C (D→I). (Found: C, 76.99; H, 8.66; N, 10.90. $C_{66}H_{88}N_8S$ requires: C, 77.29; H, 8.65; N, 10.93%). δH (270 MHz; C_6D_6): −1.27 (s, 2H), 0.92 (m, 18H), 1.2–2.0 (m, 44H), 2.1–2.4 (m, 4H), 4.03 (m, 4H), 4.49 (m, 4H), 4.60 (m, 4H), 7.66 (d, *J*=7.6 Hz, 2H), 7.74 (d, *J*=7.6 Hz, 2H), 7.83 (s, 2H), 8.03 (s, 2H); λ_{max} (cyclohexane)/nm: 336, 386, 662, 687, 705, 742.

7,10,14,17,21,24-Hexahexyl-1,3-dimethyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 8. Chromatographic separation (silica: eluent petrol) of products from reaction of 3,6-dihexylphthalonitrile (1.8 g) and 3,4-dicyano-2,5-dimethylthiophene (0.32 g) removed metal-free 1,4,8,11,15,18,22,25-octahexylphthalocyanine from the product mixture. The remaining products were rechromatographed over silica [cyclohexane–DCM (9:1) as eluent] to separate the macrocycle **8** as a blue solid, (112 mg, 5% based on 3,4-dicyano-2,5-dimethylthiophene), mp 125°C (K→D), 248°C (D→I). (Found: C, 77.73; H, 8.80; N, 10.47. $C_{68}H_{92}N_8S$ requires: C, 77.52; H, 8.80; N, 10.64%). δH (270 MHz; C_6D_6): −1.41 (s, 2H), 0.8–1.0 (m, 18H), 1.1–1.9 (m, 40H), 2.09 (s, 6H), 2.20 (m, 4H), 2.42 (m, 4H), 3.14 (m, 4H), 4.35 (t, J=6.9 Hz, 4H), 4.60 (t, J=7.1 Hz, 4H), 7.30 (d, J=7.6 Hz, 2H), 7.51 (d, J=7.6 Hz, 2H), 7.89 (s, 2H); λ_{max} (cyclohexane)/nm: 336, 674, 705, 726, 764.

Preparation of metallated tribenzo[b,g,l]thiopheno[3,4-q]porphyrazines, 6a, 7a–d

In a typical procedure, nickel(II) acetate (0.2 g) was added to a stirred solution of 7,10,14,17,21,24-hexahexyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine (**7**) (100 mg) in pentan-1-ol (20 ml) and heated under reflux for 90 min. The solvent was removed under reduced pressure and the residue purified using column chromatography over silica gel using as eluent cyclohexane–THF (5:1) and recrystallised from THF-methanol to afford *nickel(II) 7,10,14,17,21,24-hexahexyltribenzo[b,g,l]thiopheno-[3,4-q]porphyrazine **(7a)*** (86 mg, 81%) as a blue solid, mp 151°C (K→D), 267°C (D→I). FAB (LSIMS) cluster 1081 (req. 1082). (Found: C, 73.22; H, 7.89; N, 10.40. $C_{66}H_{86}N_8SNi$ requires: C, 73.25; H, 8.01; N, 10.35%). δH (270 MHz; C_6D_6): 0.91 (m, 18H), 1.05–1.85 (m, 36H), 2.15–2.35 (m, 12H), 3.95 (br t, 4H), 4.39 (br t, 4H), 4.53 (br t, 4H), 7.52 (d, J=7.6 Hz, 2H), 7.62 (d, J=7.6 Hz, 2H), 7.8 (s, 2H), 8.07 (s, 2H). λ_{max} (cyclohexane)/nm: 298, 333, 614, 681, 716.

The following were prepared similarly, in comparable yields, from the metal-free precursors and the appropriate metal acetate.

Nickel(II) 1-(6-hydroxyhexyl)-3-methyl-7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 6a. Mp 235°C (D→I). (Found: C, 74.82; H, 9.28; N, 7.92. $C_{85}H_{126}N_8OSNi$ requires: C, 74.81; H, 9.16; N, 8.21%). δH (270 MHz; C_6D_6): 0.85 (m, 18H), 1.2–2.4 (m, 81H), 3.04 (s, 3H), 3.41 (t, J=7.0 Hz, 2H), 3.75 (t, J=7.0 Hz, 2H), 3.94 (t, J=7.2 Hz, 2H), 4.21 (t, J=7.1 Hz, 2H), 4.41 (t, J=7.1 Hz, 2H), 4.53–4.66 (m, 6H), 7.48 (d, J=7.2 Hz, 1H), 7.60 (d, J=7.2 Hz, 1H), 7.67 (d, J=7.6 Hz, 1H), 7.74 (d, J=7.6 Hz, 1H), 7.84 (s, 2H); λ_{max} (cyclohexane)/nm: 300, 337, 622, 675, 693, 738.

Cobalt(II) 7,10,14,17,21,24-hexahexyltribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 7b. Mp 144°C (K→D), 302°C (D→I). FAB (LSIMS) weak cluster 1082 (req. 1083) (Found: C, 72.91; H, 8.00; N, 10.00. $C_{66}H_{86}N_8SCo$ requires: C, 73.23; H, 8.01; N, 10.35%). λ_{max} (cyclohexane)/nm: 283, 678, 714.

Zinc(II) 7,10,14,17,21,24-hexahexyltribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 7c. Mp 170°C (K→D), 337°C (D→I). FAB (LSIMS) cluster 1088 (req. 1089). (Found: C, 72.79; H, 7.96; N, 10.14. $C_{66}H_{86}N_8SZn$ requires: C, 72.80; H, 7.96; N, 10.29%). δH (270 MHz; C_6D_6 50°C): 0.91 (m, 18H), 1.3–1.6 (m, 24H), 1.7–1.9 (m, 12H), 2.2–2.5 (m, 12H), 4.04 (t, J=7.2 Hz, 4H), 4.50 (t, J=7.2 Hz, 4H), 4.70 (t, J=7.0 Hz, 4H), 7.57 (d, J=7.6 Hz, 2H), 7.67 (d, J=7.6 Hz, 2H), 7.92 (s, 2H), 8.22 (s, 2H). λ_{max} (cyclohexane)/nm: 336, 689, 726.

Copper(II) 7,10,14,17,21,24-hexahexyltribenzo[b,g,l]thiopheno[3,4-q]porphyrazine 7d. Mp 307°C (D→I). FAB (LSIMS) weak cluster 1086 (req. 1087). (Found: C, 72.85; H, 7.99; N, 10.19. $C_{66}H_{86}N_8SCu$ requires: C, 72.92; H, 7.97; N, 10.31%). λ_{max} (cyclohexane)/nm: 335, 686, 722.

Crossed cyclic tetramerisation reaction of 3,6-dioctylphthalonitrile and 2,3-dicyanothiophene. Separation of mixed benzothiopheno[2,3]porphyrazines, 9, 10 and 11

2,3-Dicyanothiophene (0.14 g) and 3,6-dioctylphthalonitrile (3.4 g) were reacted together and separated as for compound 3 above. Chromatography (silica, light petrol) separated octaoctylphthalocyanine, **1** R=C_8H_{17}, 0.75 g, as the first fraction. Petrol–DCM 4:1 separated the second fraction, *7,10,14,17,21,24-hexaoctyl-28H,30H-tribenzo[b,g,l]-thiopheno[2,3-q]porphyrazine **9*** as a blue solid (85 mg, 7% based on 2,3-dicyanothiophene), mp 171°C (K→D), 212°C (D→I). (Found: C, 78.50; H, 9.24; N, 9.39. $C_{78}H_{112}N_8S$ requires: C, 78.47; H, 9.46; N, 9.39; S, 2.69%). δH (270 MHz; C_6D_6): −1.32 (s, 2H), 0.8–1.0 (m, 18H), 1.2–1.9 (m, 56H), 1.9–2.08 (m, 2H), 2.08–2.25 (m, 2H), 2.3–2.6 (m, 12H), 4.35 (t, J=7.1 Hz, 4H), 4.58 (t, J=7.2 Hz, 4H), 4.70 (t, J=7.2 Hz, 4H), 7.54 (d, J=5.0 Hz, 1H), 7.77 (m, 4H), 7.94 (s, 2H), 8.40 (d, J=5.0 Hz, 1H); λ_{max} (THF)/nm: 340, 392, 651, 720. The next green fraction, eluent THF, was further purified by column chromatography over silica, eluent toluene, and recrystallised from THF–methanol to obtain a mixture of **11** and its isomers as a dark blue solid (20 mg, 2% based on 2,3-dicyanothiophene), mp 212°C (K→I). (Found: C, 74.12; H, 8.02; N, 11.25. $C_{60}H_{78}N_8S_2$ requires: C, 73.88; H, 8.06; N, 11.49%). δH (270 MHz; C_6D_6; 60°C): −2.75 (br d, 2H), 0.85–0.95 (m, 12H), 1.3–1.7 (m, 32H), 1.74–2.12 (m, 8H), 2.32 (m, 8H), 4.14 (m, 4H), 4.36 (m, 4H), 7.44 (m, 2H), 7.69–7.77 (m, 4H), 8.07–8.15 (m, 2H); λ_{max} (cyclohexane)/nm: 344, 593, 634, 654, 695. The final blue fraction, eluent THF–light petroleum (1:1), was recrystallised from THF–methanol to obtain a mixture of **12** and its isomers as a blue solid (6 mg, 1% based on 2,3-dicyanothiophene), mp 245°C (K→I); FAB (LSIMS) *m/z* 756. (Found: C, 66.74; H, 5.76; N, 14.53. $C_{42}H_{44}N_8S_3$ requires: C, 66.63; H, 5.86; N, 14.80%). δH (270 MHz; C_6D_6; 60°C): −3.65 (m, 2H), 0.88–0.94 (m, 6H), 1.2–1.8 (m, 16H), 1.9–2.2 (m, 4H), 2.32 (m, 4H), 4.13 (m, 4H), 7.41–7.52 (m, 5H), 8.13–8.28 (m, 3H). λ_{max} (cyclohexane)/nm: 345, 619, 645, 673, 697.

Crossed cyclic tetramerisation reaction of 2,5-didecyl-3,4-dicyanothiophene and 2,3-dicyanothiophene. Preparation of the isomer mixture of didecylthiopheno-[3,4]trithiopheno[2,3]porphyrazine, 12

3,4-Dicyano-2,5-didecylthiophene (5.24 g, 12.6 mmol) and 2,3-dicyanothiophene (0.24 g, 1.79 mmol) were reacted together using the procedure above. The first fraction to be collected from a column, eluent light petroleum–DCM

(2:1), was a mixture consisting of trace amounts of **13** and **14** and their isomers; FAB (LSIMS): clusters at 1099 and 1380. λ_{max} (THF)/nm: 326, 615, 675, 779, 820. The next green fraction, eluent hot THF, was re-chromatographed over silica gel, eluent cyclohexane–THF (2:1), and recrystallised from THF–methanol to obtain a mixture of **12** and its isomers as a blue solid (10 mg, 2% based on 2,3-dicyanothiophene); mp 209°C; FAB (LSIMS) *m/z* 818. (Found: C, 64.11; H, 6.01; N, 13.22. $C_{44}H_{50}N_8S_4$ requires: C, 64.51; H, 6.15; N, 13.68%). δH (270 MHz; C_6D_6; 50°C): −3.05 to −2.94 (m, 2H), 0.86 (br t, 6H), 1.2–1.55 (m, 20H), 1.6–1.7 (m, 4H), 1.75–1.87 (m, 4H), 2.2–2.33 (m, 4H), 3.75–3.84 (m, 4H), 7.36–7.43 (m, 3H), 7.92–7.99 (m, 1H), 8.09–8.19 (m, 2H); λ_{max} (THF)/nm: 342, 631, 664, 701, 740. Further elution of the same column with hot THF resulted in a blue fraction that appears to be tetrathiopheno[2,3]porphyrazine; λ_{max} (THF)/nm: 351, 574, 617, 632, 676.

Acknowledgements

We thank the EPSRC for a CASE studentship with Epigem (for A. J.-F.). We also thank the EPSRC Mass Spectrometry Service at Swansea for FAB (LSIMS) spectra. This work was undertaken in part as a contribution to projects run under the auspices of CEC COST programme 514 and CEC RTN contract RTN1-1999-00314.

References

1. Leznoff, C. C.; Lever, A. B. P. *Phthalocyanines—Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1989.
2. McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press: Cambridge, 1998.
3. Pandey, P. K.; Herman, C. K. *Chem. Ind.* **1998**, 739.
4. De la Torre, G.; Vázquez, P.; Aguilló-López, F.; Torres, T. *J. Mater. Chem.* **1998**, *8*, 1671.
5. See, for example, Liu, Y.; Xu, Y.; Zhu, D.; Wada, T.; Sasabe, H.; Liu, L.; Wang, W. *Thin Solid Films* **1994**, *244*, 943; Liu, Y.; Xu, Y.; Zhu, D.; Wada, T.; Sasabe, H.; Zhao, Z.; Xie, X. *J. Phys. Chem.* **1995**, *99*, 6957.
6. Kobayashi, N.; Kondo, R.; Nakajima, S.-I.; Osa, T. *J. Am. Chem. Soc.* **1990**, *112*, 9640.
7. Kudrevich, S. V.; Gilbert, S.; van Lier, J. E. *J. Org. Chem.* **1996**, *61*, 5706.
8. Yokote, M.; Shibamiya, F. *Kogyo Kagaku Zasshi* **1959**, *62*, 224. *Chem. Abstr.* **1961**, *55*, 24019; Yokote, M.; Shibamiya, F.; Hayakawa, H. *Yuki-Gosei Kagaka Kyokai-Shi* **1965**, *23*, 151. *Chem. Abstr.* **1965**, *71*, 38931h; Sakamoto, K.; Shibamiya, F. *J. Jpn. Soc. Colour Material* **1985**, *58*, 121; Sakamoto, K.; Shibamiya, F. *J. Jpn. Soc. Colour Material* **1986**, *59*, 517.
9. Cook, M. J.; Jafari-Fini, A. *J. Mater Chem.* **1997**, *7*, 2327.
10. Bakboord, J.; Cook, M. J.; Hamuryudan, E. *J. Porphyrins Phthalocyanines* **2000** (in press).
11. Cherodian, A. S.; Davies, A. N.; Richardson, R. M.; Cook, M. J.; McKeown, N. B.; Thomson, A. J.; Feijoo, J.; Ungar, G.; Harrison, K. L. *Mol. Cryst. Liq. Cryst.* **1991**, *196*, 103; Cook, M. J.; Cracknell, S. J.; Harrison, K. J. *J. Mater. Chem.* **1991**, *1*, 703; Belushkin, A. V.; Cook, M. J.; Frezzato, D.; Haslam, S. D.; Ferrarini, A.; Martin, D.; McMurdo, J.; Nordio, P. L.; Richardson, R. M.; Stafford, A. *Mol. Phys.* **1998**, *93*, 593.
12. Kobayashi, N.; Konami, H. In *Phthalocyanines—Properties and Applications*, Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1996; Vol. 4 (pp 343).
13. Linstead, R. P.; Noble, E. G.; Wright, J. M. *J. Chem. Soc.* **1937**, 911.
14. Knawby, D. M.; Swager, T. M. *Chem. Mater.* **1997**, *9*, 535.
15. For a preliminary communication of aspects of this work see Cook, M. J.; Jafari-Fini, A. *J. Mater Chem.* **1997**, *7*, 5.
16. McKeown, N. B.; Cook, M. J.; Chambrier, I. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1169.
17. Chambrier, I.; Cook, M. J.; Cracknell, S. J.; McMurdo, J. *J. Mater. Chem.* **1993**, *3*, 841.
18. Morel, J.; Paulmier, C.; Pastour, P. C. R. *Acad. Sci. Paris, Ser. C* **1968**, *266*, 1300.
19. Vegh, D.; Landl, M.; Pavlovicova, R.; Kuzmany, H.; Zalupsky, P. *Khimiya Geterotsiklicheskikh Soedinenii* **1995**, 1409.
20. Cook, M. J.; McMurdo, J.; Miles, D. A.; Poynter, R. H.; Simmons, J. M.; Haslam, S. D.; Richardson, R. M.; Welford, K. *J. Mater. Chem.* **1994**, *4*, 1205.
21. Critchley, S. M.; Willis, M. R.; Cook, M. J.; McMurdo, J.; Maruyama, Y. *J. Mater. Chem.* **1992**, *2*, 157; Cook, M. J.; Mayes, D. A.; Poynter, R. H. *J. Mater. Chem.* **1995**, *5*, 2233.
22. Bryant, G. C.; Cook, M. J.; Ryan, T. G.; Thorn, A. J. *Tetrahedron* **1996**, *52*, 809.
23. Byron, D.; Matharu, A.; Wilson, R.; Wright, G. *Mol. Cryst. Liq. Cryst.* **1995**, *265*, 61.