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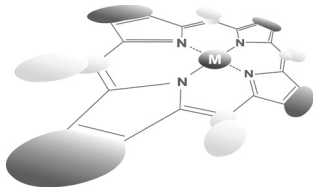

Routes to some 3,6-disubstituted phthalonitriles and examples of phthalocyanines derived therefrom. An overview

Martin J. Heeney[§], Shaya A. Al-Raqa[ξ], Aurélien Auger[ж], Paul M. Burnham, Andrew N. Cammidge, Isabelle Chambrier* and Michael J. Cook*[◊]

School of Chemistry, University of East Anglia, Norwich NR4 7TJ, United Kingdom

Dedicated to Professor Evgeny Luk'yanets on the occasion of his 75th birthday

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ABSTRACT: The paper reviews a selection of synthetic pathways that provide access to 3,6-disubstituted phthalonitriles, precursors for the synthesis of 1,4,8,11,15,18,22,25-octasubstituted phthalocyanine derivatives. Early routes using Diels–Alder reactions for the synthesis of 3,6-dialkyl, 3,6-dialkoxymethyl, 3,6-dialkenyl and 3,6-diphenylphthalonitriles are appraised. However, the emphasis of the review focuses on the scope and applications of 2,3-dicyanohydroquinone as a starting material for obtaining 3,6-disubstituted phthalonitriles. The earliest example of the use of 2,3-dicyanohydroquinone concerned its O-alkylation to afford 3,6-dialkoxyphthalonitriles. These are immediate precursors to near-infrared absorbing phthalocyanine derivatives. Triflation of 2,3-dicyanohydroquinone extends the scope of the compound for phthalocyanine synthesis; the bis-triflate derivative is susceptible to S_NAr reactions and readily reacts with thiols to provide 3,6-bis(alkylsulfanyl) and 3,6-bis(arylsulfanyl)-phthalonitriles. 3,6-Bis(phenylselenyl)phthalonitrile has also been obtained recently from the same precursor. Phthalocyanine derivatives obtained from them typically show a strongly bathochromically shifted Q-band absorption that is particularly sensitive to the central metal ion. The bis-triflate of 2,3-dicyanohydroquinone is also an ideal precursor for participation in cross-coupling reactions. Examples from the University of East Anglia group and elsewhere are presented which show the application of the nickel-catalyzed Negishi coupling reaction using alkylzinc halide derivatives. Yields of 3,6-dialkylphthalonitriles and 3,6-bis(substituted alkyl)phthalonitriles range from *ca*. 40 to 70%. Direct comparison for one example shows that the yield from the Negishi coupling method is higher than that using the Suzuki coupling protocol. Examples of the preparation of 3,6-diarylphthalonitriles from 2,3-dicyanohydroquinone bis-triflate using the Suzuki coupling reaction are reported with yields of the order of 65–70%. The review also includes a further application of 2,3-dicyanohydroquinone as a precursor to both monobromo and dibromo derivatives of 3,6-dibutoxyphthalonitrile. These compounds provide opportunities for cross-coupling at the brominated sites to provide more complex derivatives with the potential to serve as precursors of highly substituted phthalocyanine derivatives.

KEYWORDS: 2,3-dicyanohydroquinone, 1,4,8,11,15,18,22,25-octakis(alkylsulfanyl)phthalocyanines, mixed substituent phthalocyanines, near-infrared absorbing dyes, Negishi coupling, Suzuki coupling.

[◊]SPP full member in good standing

*Correspondence to: Isabelle Chambrier, email: I.Fernandes@uea.ac.uk; Michael J. Cook, email: m.cook@uea.ac.uk
Current addresses: [§]Martin J. Heeney, Department of Chemistry, Imperial College, South Kensington Campus, Exhibition Rd, London SW7 2AZ, United Kingdom. [ξ]Shaya A. Al-Raqa, Chemistry Department, Faculty of Science, Taibah University, P.O. Box 3002, Al-Madinah Al-Munawrah, Saudi Arabia. [ж]Aurélien Auger, CEA-Grenoble, DRT/LITEN/DTNM/LCSN, C2/459, 17 rue des Martyrs, 38054 Grenoble Cédex 9, France

INTRODUCTION

A long standing interest of the Materials Chemistry group at the University of East Anglia (UEA) has been the development of phthalocyanines and related derivatives. The primary aims have aspired to develop phthalocyanine chemistry and to exploit the properties of examples of the macrocycle within a number of fields of research [1]. The latter include the use of thin film formulations for gas sensing [2–6] and various other device applications [7–12], as well as in formulations for photodynamic therapy protocols [13–20]. The research has been "synthesis led" by which we mean that compounds generally have been purpose designed for individual projects. For various reasons discussed elsewhere [1], we have favored the preparation of single component phthalocyanine products from the classic cyclotetramerisation reactions of phthalonitrile precursors, rather than mixtures of regioisomers. This led us to focus on the use of 3,6-disubstituted phthalonitriles as precursors which provide access to 1,4,8,11,15,18,22,25-(or non-peripheral) octasubstituted phthalocyanines [1]. In our experience this substitution pattern has led to phthalocyanine derivatives with greater solubility and lower propensity to aggregate in solution than examples of isomers where substituents are located at the 2,3,9,10,16,17,23,24-(or peripheral) sites.

The present review focuses on our development of synthetic routes to various classes of 3,6-disubstituted phthalonitriles. This includes a summary of our early work using Diels–Alder based routes and also our growing emphasis on the use of 2,3-dicyanohydroquinone as a precursor. The material presented here, particularly that which exploits the use of 2,3-dicyanohydroquinone, draws together piecemeal reports in various refereed journals and data included in a 2001 Patent Application [21]. Examples of synthetic methodologies are gathered in the Experimental section of this paper. Also included in this review is a small selection of published and unpublished phthalocyanine derivatives that have been obtained from various 3,6-disubstituted phthalonitriles described in this paper.

3,6-DISUBSTITUTED PHTHALONITRILES *VIA* DIELS–ALDER PROTOCOLS

In our work undertaken during the 1980s and 1990s, we were interested in developing a route for the synthesis of 3,6-dialkyl, 3,6-bis-functionalised alkyl, and 3,6-dialkoxymethylphthalonitriles as potential precursors to liquid crystalline phthalocyanines and phthalocyanines appropriate for LB film work [1]. This substitution pattern is not realistically available using simple electrophilic substitution methods and at that time we turned to Diels–Alder based approaches. Our original scheme (Fig. 1), utilized furans as precursors [22, 23]. Apart from preparing simple 2,5-dialkylfuran derivatives as precursors for 3,6-dialkylphthalonitriles, conditions were found to alkylate sequentially the 2- and 5- ring positions which allowed different groups *i.e*. an alkyl and a functionalised alkyl group to be incorporated to provide access to compounds such as 2-alkyl-5-hydroxyalkylfurans [24]. These particular furan derivatives served as precursors of 3-alkyl-6-hydroxyalkylphthlonitriles. The latter proved useful for cross condensation with 3,6-dialkylphthalonitriles to form interestingly functionalized phthalocyanines that could be linked together [25, 26]. We also used other readily available functionalized furans such as 2,5-bis-hydroxymethyl furan to prepare 2,5-dialkoxymethylfurans and thence 3,6-bis(alkylmethoxy)phthalonitriles [27]. Though a large number of phthalonitrile compounds were obtained satisfactorily the method suffers from the fact that the Diels-Alder reaction of furans with fumaronitrile

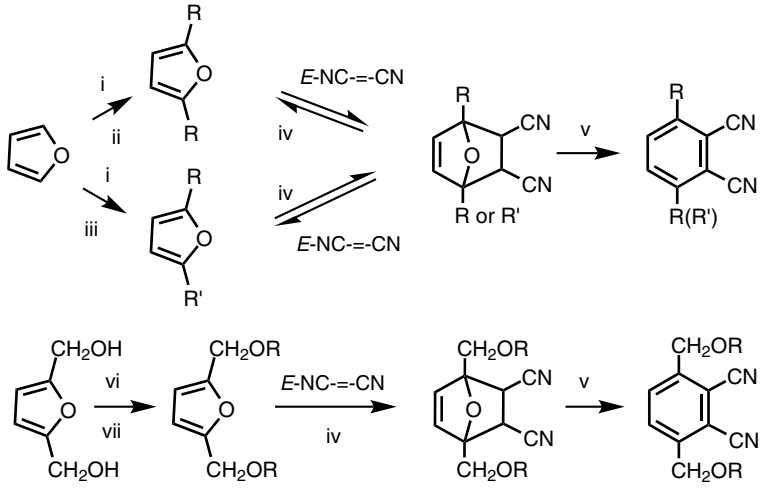


Fig. 1. Application of Diels–Alder reactions using furan and fumaronitrile to access examples of 3,6-dialkylphthalonitriles. R and R′ refer to different alkyl or functionalised alkyl groups. i. RX/BuLi; ii. second reaction RX, BuLi; iii. BuLi/R′X where R′ ≠ R; iv. rt or lower; v. $LiN(SiMe_3)_2$; vi. $SOCl_2$; vii. RO^-

is both slow, *ca*. 10 days, and reversible. Entropy factors dictate that conversion to the adduct is enhanced at low temperatures but then the cycloaddition reaction becomes slower still; furthermore, a systematic study of the reaction showed that as the length of the alkyl chain is increased the equilibrium contains less of the adduct [28].

Improved access to symmetrically substituted 3,6-dialkylphthalonitriles was achieved using Diels–Alder reactions on 2,5-dialkylthiophene-1,1-dioxide derivatives as indicated in Fig. 2. Yields of phthalonitriles are overall higher than when using furan compounds but the need for an oxidation step provides limitations regarding extension of the scheme to oxidation-sensitive substituent groups. Nevertheless the protocol has proved to be one of our basic tools to prepare the symmetrically substituted 3,6-dialkylphthalocyanines [23, 29]. A wide range of compounds were prepared with alkyl groups as long as hexadecyl [29]. These have proved important for our research into phthalocyanine materials [1].

Elsewhere, Luk'yanets' group had been exploring Diels–Alder protocols to give phthalonitriles from reactions of cyclopentadienones with chloromaleonitrile [30] and reactions of substituted dienes with dichlorofumaronitrile (or dichloromaleonitrile/dichlorofumaronitrile mixtures) [31]. The latter approach, using 1,4-diphenyl-1,3-butadiene, afforded 3,6-diphenylphthalonitrile in 73% yield (Fig. 3).

3,6-DISUBSTITUTED PHTHALONITRILES *VIA* 2,3-DICYANOHYDROQUINONE

General scheme

To our knowledge, 2,3-dicyanohydroquinone is the only readily available 1,2,3,4- tetrasubstituted benzene derivative bearing nitrile groups at adjacent positions. It is, therefore, a potentially useful precursor to 3,6-disubstituted phthalonitriles of types **1–6** shown in Fig. 4 and thence non-peripheral octasubstituted phthalocyanines. Figure 4 also shows the generalized scheme that we and others have used to prepare these phthalocyanine precursors; each pathway is discussed in the sections that follow.

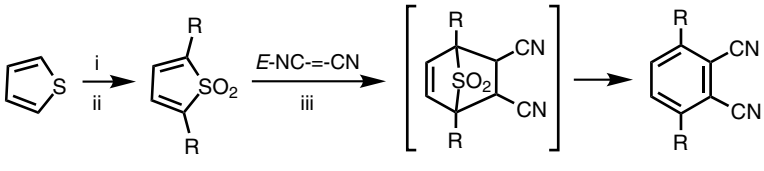


Fig. 2. Application of Diels–Alder reactions using thiophene-1,1-dioxides to access examples of 3,6-dialkylphthalonitriles. (i) RI/BuLi; (ii) Sodium perborate; (iii) *ca*. 150 °C sealed tube

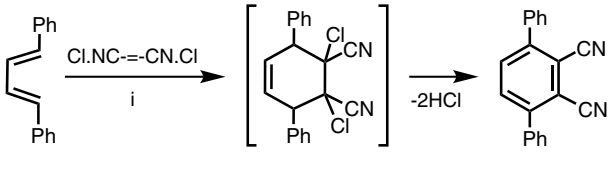


Fig. 3. Application of a Diels–Alder reaction using a 1,3-diene to access 3,6-diphenylphthalonitrile. i. 180–185 °C for 2 h

3,6-Dialkoxyphthalonitriles (series 1)

Perhaps the earliest report of the use of 2,3-dicyanohydroquinone as a precursor of useful 3,6-disubstituted phthalonitriles for phthalocyanine synthesis was described by Witkievic, Dabrowski and Waclawek in 1976 [32]. The synthesis commenced with the methylation of 2,3-dicyanohydroquinone to form 3,6-dimethoxyphthalonitrile, see Fig. 4, left hand side. Cyclotetramerisation of the compound generated the non-peripheral octakis(methoxy)phthalocyanine ligand and various metalated derivatives were obtained, see structure **7** (Fig. 5), R = Me. The authors subsequently undertook electrical measurements on the compounds and investigated them as catalysts.

The UEA group's first synthesis of novel phthalocyanine compounds was directed at obtaining long chain homologs of octakis(methoxy)phthalocyanine, *i.e*. further examples of series **7**. These synthetic targets were chosen in expectation of their higher solubility in organic solvents and indeed were used for Langmuir–Blodgett film deposition studies and for doping into calamitic liquid crystal formulations. The precursor 3,6-dialkoxyphthalonitriles were obtained using the Williamson's ether synthesis employed by Witkievic *et al*. [32]. The substituents investigated ranged from ethoxy through to decyloxy as well as 4-pentenyloxy, 3-phenylpropyloxy and *iso*-pentyloxy [33]. Yields of the phthalonitriles were of the order of 35–58%. These were then converted into the phthalocyanines, series **7**, using the conventional LiOR/ROH base catalyzed conditions. However, we found that *trans*-etherification tended to occur and that, to overcome the outcome of this process, the chainlength of the alcohol/lithium alkoxide should be that of the alkyl chain of the haloalkane. Apart from the use of these phthalocyanine derivatives in Langmuir–Blodgett (LB) film studies [34], they also provided our first examples of far-red/near-infrared absorbers. Thus they exhibited the Q-band in the region λ_{max} 738 and 760 nm for the metal-free derivatives in toluene and at 752, 748 and 742 nm for the single Q-band of a Cu, Zn and Ni derivative respectively in dichloromethane.

3,6-Bis(alkylsulfanyl)phthalonitriles (series 2), 3,6-bis(arylsulfanyl)phthalonitriles (series 3) and 3,6-bis(arylselenyl)phthalonitrile (compound 4)

We first investigated the synthesis of these 3,6-disubstituted phthalonitriles of series **2** and **3**, see Fig. 4,

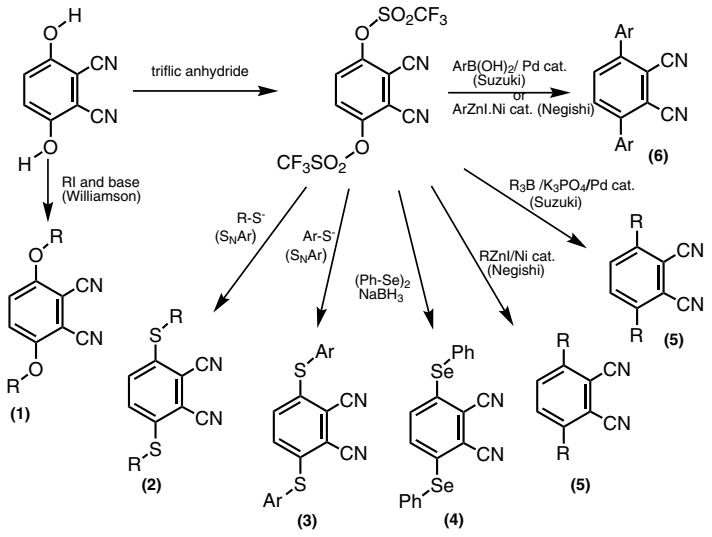


Fig. 4. Examples of classes of 3,6-disubstituted phthalonitrile derivatives available from 2,3-dicyanohydroquinone. R = alkyl; Ar = aryl. Novel examples of compounds of series **2** and **3** reported in this paper can be found in Tables 1 and 2. Novel and known examples of series **5** and **6** prepared by the routes shown are collected in Table 3

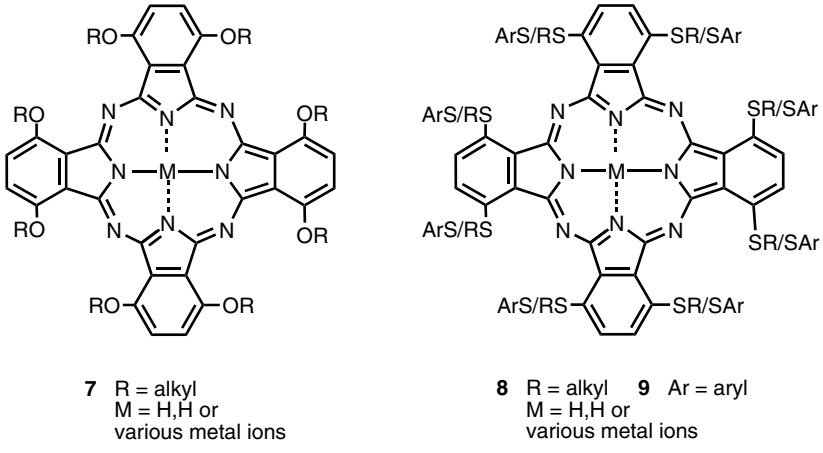


Fig. 5. Structures of series **7**, **8** and **9**. Novel examples of series **8** and **9** showing substituents and M ions and their characterization data are collected in Tables 1 and 2

ca. 2000 and published a preliminary communication of a few examples in 2003 [35]; these and other analogs are referred to in a 2001 patent application [21] and are now collected, with characterization data, in Tables 1 and 2. The synthetic scheme exploits the triflate derivative of 2,3-dicyanohydroquinone (Fig. 4). The methodology developed at UEA reacts 2,3-dicyanohydroquinone bis-triflate with an appropriate thiol in the presence of an excess of finely crushed potassium carbonate in DMF. Typically, in our hands, the reaction is stirred for *ca*. 72 h to yield the 3,6-bis(alkylsulfanyl)phthalonitriles or 3,6-bis(arylsulfanyl)phthalonitriles (Tables 1 and 2).

These compounds were converted into the corresponding 1,4,8,11,15,18,22,25-octakis(alkylsulfanyl or arylsulfanyl) phthalocyanines, series **8** and **9**, and examples of zinc, magnesium, copper, lead and chloroindium metalated derivatives, Fig. 5, and their characterization data are collected in Tables 1 and 2 and the Experimental. Also prepared was an example of a bis(phthalocyanine)-cerium(IV) sandwich compound **10**, Fig. 6.

The examples of the phthalocyanines of series **8** and **9** listed in the tables exhibit a more significant bathochromic shift of the Q-band than found in series **7**, ranging from 772–848 nm. Kobayashi and coworkers account for this in terms of the large MO coefficient of the HOMO at the site of substitution causing the electron-donating groups to destabilize the HOMO energy [36]. A further feature of the data in Tables 1 and 2 is that the Q-band λ_{max} is sensitive to the metal ion and this, together with bathochromic shifts of higher energy bands, leads to a set

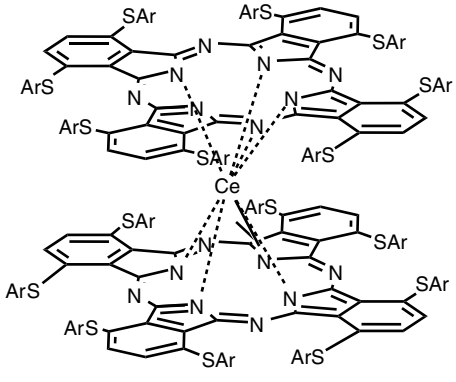
Table 1. Conversion of 2,3-dicyanohydroquinone bis-triflate into 3,6-bis(alkylsulfanyl)phthalonitriles, series **2**, and their conversion into metalated 1,4,8,11,15,18,22,25-octakis(alkylsulfanyl)phthalocyanines (series **8**)

Groups	3,6-bis(alkylsulfanyl)phthalonitrile Series **2**			1,4,8,11,15,18,22,25-(alkylsulfanyl)$_8$ MPc Series **8**				
Alkyl-S	#	Yield % mp	Formula and CHN Found & (Required) C H N	#	Yield, %	Formula and CHN Found & (Required) C H N	^{1}H NMR (d_6-benzene + 1% d_5-pyridine): δ, ppm	λ_{max}, nm ($\varepsilon \times 10^{-5}$) THF
$C_6H_{13}S$	**2a**	70 82–83°	$C_{20}H_{28}N_2S_2$ 66.60 7.81 7.83 (66.62 7.72 7.77)	**8a**	33	$C_{80}H_{112}N_8S_8Zn$ 63.84 7.43 7.49 (63.73 7.37 7.43)	0.89 (t, 24H), 1.33 (m, 32H), 1.58 (m, 16H), 1.97 (m, 16H), 3.30 (t, 16H), 7.81(s, 8H)	781 (1.56)
				8b	67	$C_{80}H_{112}N_8S_8Mg$ 65.51 7.60 7.64 (65.52 7.70 7.64)	0.89 (t, 24H), 1.25–1.45 (m, 32H), 1.57–1.65 (m, 16H), 2.00 (m, 16H), 3.34 (t, 16H), 7.83 (s, 8H)	773
				8c	15	$C_{80}H_{112}N_8S_8Pb$ 58.29 6.65 6.65 (58.25 6.84 6.79)	0.85 (t, 24H), 1.32 (m, 32H), 1.53–1.64 (m, 16H), 1.91–2.00 (m, 16H), 3.27 (t, 16H), 7.76 (s, 8H)	818 (1.00)
				8d	20	$C_{80}H_{112}N_8S_8InCl$ 60.66 7.11 6.84 (60.33 7.09 7.04)	0.90 (t, 24H), 1.32–1.45 (m, 32H), 1.55–1.65 (m, 16H), 1.87–1.96 (m, 16H), 3.23 (t, 16H), 7.79 (s, 8H)	836 (2.41)
				8e	55	$C_{80}H_{112}N_8S_8Cu$ 63.39 7.53 7.31 (63.73 7.48 7.43)	—	783 (1.56)
$C_7H_{15}S$	**2b**	46 —	$C_{22}H_{32}N_2S_2$ 67.50 8.21 7.07 (68.01 8.31 7.21)	**8f**	11	$C_{88}H_{128}N_8S_8Zn$ 65.25 8.03 6.78 (65.32 7.98 6.93)	0.89 (t,24H), 1.30 (m,48H), 1.60 (m,16H), 1.99 (m,16H), 3.30 (t,16H), 7.81 (s,8H)	779 (1.36)
$C_8H_{17}S$	**2c**	27 91–92°	$C_{24}H_{36}N_2S_2$ 69.20 8.74 6.56 (69.19 8.72 6.73)	**8g**	12	$C_{96}H_{144}N_8S_8Zn$ 66.74 8.51 6.48 (66.63 8.39 6.48)	0.90 (t, 24H), 1.30 (m, 64H), 1.62 (m, 16H), 2.01(m, 16H), 3.34 (t, 16H), 7.84 (s, 8H)	781 (1.45)
				8h	48	$C_{96}H_{144}N_8S_8Mg$ 68.29 8.69 6.50 (68.18 8.58 6.63	0.91 (t, 24H), 1.25–1.52 (m, 64H), 1.57–1.68 (m, 16H), 2.03 (m, 16H), 3.37 (t, 16H), 7.86 (s, 8H)	774
$C_9H_{19}S$	**2d**	65 86–88°	$C_{26}H_{40}N_2S_2$ 70.11 8.91 6.10 (70.22 9.07 6.30)	**8i**	15	$C_{104}H_{160}N_8S_8Zn$ 67.69 8.71 5.91 (67.73 8.74 6.08)	0.89 (t, 24H), 1.19–1.55 (m, 80H), 1.60–1.67 (m, 16H), 2.04 (m, 16H), 3.40 (t, 16H), 7.87 (s, 8H)	782
				8j	62	$C_{104}H_{160}N_8S_8Mg$ 69.44 8.76 5.99 (69.27 8.94 6.21)	0.90 (t, 24H), 1.18–1.52 (m, 80H), 1.59–1.67 (m, 16H), 2.04 (m, 16H), 3.38 (t, 16H), 7.86 (s, 8H)	772
$C_{10}H_{21}S$	**2e**	68 —	$C_{28}H_{44}N_2S_2$ 71.31 9.38 5.85 (71.14 9.39 5.93)	**8k**	65	$C_{112}H_{176}N_8S_8Zn$ 69.01 9.05 5.71 (68.76 9.07 5.73)	0.90 (t, 24H), 1.18–1.52 (m, 96H), 1.58–1.68 (m, 16H), 2.01–2.11 (m, 16H), 3.38 (t, 16H), 7.86 (s, 8H)	781
				8l	69	$C_{112}H_{176}N_8S_8Mg$ 70.36 9.38 5.77 (70.23 9.26 5.85)	0.90 (t, 24H), 1.26–1.52 (m, 96H), 1.58–1.68 (m, 16H), 2.05 (m, 16H), 3.38 (t, 16H), 7.86 (s, 8H)	776
$C_{11}H_{23}S$	**2f**	63 92–93°	$C_{30}H_{48}N_2S_2$ 71.53 9.62 5.40 (71.94 9.66 5.59)	**8m**	33	$C_{120}H_{192}N_8S_8Zn$ 69.64 9.33 5.39 (69.97 9.35 5.42)	0.91 (t, 24H), 1.20–1.52 (m, 112H), 1.60–1.68 (m, 16H), 2.01–2.10 (m, 16H), 3.37 (t, 16H), 7.86 (s, 8H)	781

Table 2. Conversion of 2,3-dicyanohydroquinone bis-triflate into 3,6-bis(arylsulfanyl)phthalonitriles, series **3**, and thence to 1,4,8,11,15,18,22,25-octakis(arylsulfanyl)phthalocyanine derivatives series **9** and compound **10**

Substituent	3,6-Bis(arylsulfanyl)phthalonitrile Series **3**			1,4,8,11,15,18,22,25-(arylsulfanyl)$_8$ MPc Series **9** and compound **10**				
Aryl-S	#	Yield % mp	Formula and CHN Found & (Required) C H N	#	Yield, %	Formula and CHN Found & (Required) C H N	^{1}H NMR(d_6-benzene): δ, ppm	λ_{max}, nm ($\varepsilon \times 10^{-5}$) THF
PhS	**3a**	65 107–110°	$C_{20}H_{12}N_2S_2$ 69.78 3.47 8.29 (69.74 3.51 8.13)	**9a**	19	$C_{80}H_{48}N_8S_8Zn$ 66.34 3.46 7.70 (66.57 3.35 7.76)	7.12 (s, 8H), 7.38–7.43 (m, 24H), 7.63–7.83 (m, 16H)	779 (1.62)
				9b	28	$C_{80}H_{48}N_8S_8Pb$ 60.75 3.32 6.86 (60.62 3.52 7.07)	7.13 (s, 8H), 7.40–7.44 (m, 24H), 7.75–7.77 (m, 16H)	8.16 (0.75)
				9c	46	$C_{80}H_{48}N_8S_8InCl$ 63.09 3.31 7.20 (62.88 3.17 7.33)	7.21 (s, 8H), 7.38–7.49 (m, 24H), 7.72–7.84 (m, 16H)	8.34 (1.01)
4-MePhS	**3b**	86 167–169°	$C_{22}H_{16}N_2S_2$ 70.84 4.28 7.64 (70.94 4.33 7.52)	**9d**	14	$C_{88}H_{64}N_8S_8Zn$ 67.36 4.27 7.18 (67.96 4.15 7.20)	2.48 (s, 24H), 7.09 (s, 8H), 7.17 (d, 16H), 7.65 (d, 16H)	787 (1.58)
				9e	37	$C_{80}H_{64}N_8S_8Pb$ 62.08 3.83 6.59 (62.28 3.80 6.60)	2.41 (s, 24H), 7.08 (s, 8H), 7.25 (d, 16H), 7.66 (d, 16H)	824 (1.26)
				9f	10	$C_{80}H_{64}N_8S_8InCl$ 64.34 4.09 6.70 (64.44 3.93 6.83)	2.42 (s, 24H), 7.14 (s, 8H), 7.27 (d, 16H), 7.69 (d, 16H)	848 (1.29)
4-t-BuPhS	**3c**	94 191–192°	$C_{28}H_{28}N_2S_2$ 73.53 6.18 6.03 (73.64 6.18 6.13)	**9g**	20	$C_{112}H_{112}N_8S_8H_2$ 73.53 6.28 6.15 (73.56 6.26 6.12)	0.36 (s, 2H), 1.24 (s, 72H), 7.24 (d, 16H), 7.50 (s, 8H), 7.91 (d, 16H)	810
				10	15	$C_{224}H_{224}N_8S_8Ce$[a] 70.75 5.86 5.84 (70.92 5.95 5.91)	1.37 (s, 144H), 7.15 (s, 16H), 7.47 (d, 32H), 7.72 (d, 32H)	754

[a] See Fig. 6.



10 Ar = 4-t-BuPh

Fig. 6. Structure of the cerium metalated bis-phthalocyanine complex **10**. See Table 2

of variously colored phthalocyanine dyes among which the lead metalated derivative **8c**, Q-band λ_{max} 818 nm, proved to be the first published red phthalocyanine [35].

A number of recent publications from other laboratories have also focused on this class of phthalocyanine compound, extending the range of derivatives shown in Tables 1 and 2. Thus Nyokong and coworkers prepared the octakis(pentylsulfanyl) and (octylsulfanyl) phthalocyanine analogues with tantalum(III) hydroxide as the central ion for electrochemical studies [37], the octylsulfanyl and dodecylsulfanyl analogues with palladium as the central metal for photooxidation of nitrobenzene on single wall carbon nanotubes [38], and the Mn(II) acetate and Co complexes of the hexylsulfanyl substituted ligand for electrochemical and electrocatalytic studies [39]. Sakamoto and coworkers [40] have extended the range of octa(arylsulfanyl) substituted

phthalocyanines, where "aryl" is methoxyphenyl, tolyl or 4-t-butylphenyl, incorporating copper, cobalt, nickel, zinc and lead as the central metal.

In an intriguing development, Kobayashi *et al*. recently synthesized the octa(phenylsulfanyl)phthalocyanine containing $P(OMe)_2 \cdot [PF_6]$. This was to achieve an added shift of the Q-band to lower energy arising from the large electronegativity of phosphorus enhanced by the electron withdrawing effect of the +5 oxidation state. The strategy provided a compound that exhibits a Q-band at 1018 nm. The same group also prepared 3,6-bis(phenylselenyl)phthalonitrile, compound **4**, using the route indicated in Fig. 4, as precursor for the corresponding octakis(phenylselenyl)phthalocyanine, a compound exhibiting a Q-band λ_{max} 1033 nm [41].

3,6-Dialkylphthalonitriles (series 5)

Alternatives to Diels–Alder based approaches to obtain these derivatives, described above, became evident as groups elsewhere, unconnected with macrocyclic chemistry, were developing new methodologies for C–C bond forming reactions catalyzed by metal complexes [42, 43]. Some of these were evidently applicable for accessing 3,6-dialkylphthalonitriles and we sought to investigate this type of approach *ca*. 2000 [21]. The first method we investigated was the Ni catalysed Negishi cross-coupling reaction between the bis-triflate of dicyanohydroquinone and alkylzinc reagents, see right hand side of Fig. 4. As a model, the first cross-coupling was undertaken using decylzinc iodide as reagent. The Ni(0) catalyst $Ni(PPh_3)_4$ was generated *in situ* by treatment of $NiCl_2(PPh_3)_2$ and PPh_3 with *n*-BuLi. Substrate and reagent were added and after 16 h a yield of 60–70% of 3,6-didecylphthalonitrile, (**5i**) in Table 3, was recovered. The same conditions were then used to prepare 1,1-H-2,2-H-perfluorodecylphthalonitrile (**5k**) using 1,1-H-2,2-H-perfluorodecylzinc iodide as reagent and 3,6-di(4-pivaloylbutyl)phthalonitrile (**5l**) using 4-pivaloylbutylzinc iodide. As a further development, the same procedure was applied using 6-chlorohexylzinc bromide to yield 3,6-di(6′-chlorohexyl)phthalonitrile (**5m**). The yield of the reaction was 61%. The introduction of halogenated chains is not readily possible using the furan or thiophene routes above because of the use of a strong base in the first steps of the schemes. Of course, the terminal chloro functionality can be displaced with various nucleophiles to provide more complex phthalonitrile derivatives. Further examples of the use of the above Negishi coupling protocol, taken from published papers [44, 45], are included in Table 3.

Attention was then given to application of the Suzuki reaction which involves cross-coupling of an aryl compound with an alkylboron derivative in the presence of a Pd catalyst. As a trial we sought to prepare once again the 3,6-didecylphthalonitrile (**5i**). The most successful reaction conditions that were established utilised the *in situ* formation of tridecylborane from borane and 1-decene. Base was added to form the borate complex. To this, $PdCl_2$(dppf) was added as catalyst along with dicyanohydroquinone bis-triflate. After a 10 h heating to reflux and work-up, 3,6-didecylphthalonitrile was isolated. The yields proved to be sensitive to the added base. Thus a yield of 38% was recovered from the reaction using K_3PO_4 but was lower, 28%, when K_2CO_3 was used. Neither yield matched that of the Negishi coupling reaction which has now become our method of choice for the synthesis of 3,6-dialkylphthalonitriles, at least for small scale preparations. Table 3 reports yields of various coupling reactions.

Table 3. Conversion of 2,3-dicyanohydroquinone bis-triflate into 3,6-disubstituted phthalonitriles, series **5** and **6**, using (a) Negishi coupling or (b) Suzuki coupling. Characterization data for novel derivatives (this work) are found in the Experimental section

#	3/6 substituents	Coupling method	Yield, %	Ref. if not this work
5a	Pentyl	a	56	—
5b	3-Methylbutyl	a	72	44
5c	4-Methylpentyl	a	69	44
5d	5-Methylhexyl	a	63	44
5e	Hexyl	a	68	—
5f	Cyclopentylmethyl	a	45	45
5g	Cyclohexylmethyl	a	41	45
5h	6-Methylheptyl	a	66	44
5i	Decyl	a	63–70	—
5i	Decyl	b	38	—
5j	S-3,7-dimethyloctyl	a	68	44
5k	1,1-H-2,2-H-perfluorodecyl	a	58	—
5l	4-Pivaloylbutyl	a	62	—
5m	6-Chlorohexyl	a	61	—
6a	Phenyl	b	88	—
6b	4-t-Butylphenyl	b	36	—
6c	4-Methoxyphenyl	b	73	—
6c	4-Methoxyphenyl	a	67	—
6d	3-Methoxyphenyl	b	73	—
6d	3-Methoxyphenyl	a	66	—
6e	2-Methoxyphenyl	b	20	—
6e	2-Methoxyphenyl	a	30	—
6f	3,5-Dimethylphenyl	b	25	46
6g	Thiophen-3-yl	b	47	46
6h	Furan-2-yl	b	51	46

3,6-Diarylphthalonitriles (series 6)

The application of cross-coupling approaches was then extended to the syntheses of 3,6-diarylphthalocyanines, Table 3. We first investigated the application of the Suzuki reaction by reacting phenylboronic acid with dicyanohydroquinone bis-triflate in the presence of $Pd(PPh_3)_4$ as catalyst to provide the known 3,6-diphenylphthalonitrile (**6a**) in 79% yield. 3,6-Bis(4-t-butylphenyl)-phthalonitrile (**6b**) was prepared similarly. The syntheses of 3,6-bis(4-methoxyphenyl)phthalonitrile(**6c**),3,6-bis(3-methoxyphenyl)phthalonitrile (**6d**) and 3,6-bis(2-methoxyphenyl)phthalonitrile (**6e**) were undertaken by both Suzuki and Negishi coupling procedures for comparative purposes. Yields recovered were broadly similar from the two approaches, Table 3. See also the Experimental section. One of the present authors, Al-Raqa, has independently employed the Suzuki conditions satisfactorily to prepare 3,6-bis(heteroaryl)phthalonitriles [46], compounds (**6g**) and (**6h**) in Table 3.

Mixed aryl and alkyl non-peripherally octasubstituted phthalocyanines (series 11 and 12)

The UEA group has for a long time been interested in the synthesis of non-uniformly substituted phthalocyanines, such as amphiphilic materials bearing a combination of hydrophobic and hydrophilic groups for deposition as LB films or materials bearing a thiol/disulfide terminated alkyl group for SAM film studies [1]. These were synthesized through an initial mixed cyclotetramerisation reaction of two different 3,6-disubstituted phthalonitrile precursors, where the groups were alkyl or functionalized alkyl. Examples have been reviewed elsewhere [1]. A key to the ready accessibility of these non-uniformly substituted phthalocyanines has been the ease of separation of the cross-condensation products. This arises largely because of their marked solubility in organic solvents and a limited propensity for self-aggregation, both features that simplify column chromatographic separation and purification. In light of the ready availability of series of both 3,6-dialkyl and 3,6-diarylphthalonitriles a short program to synthesize so-called 3:1 or AAAB type compounds, Fig. 7, was developed to provide materials initially for potential PDT applications. When A is used in excess then the principal components of the product mixture are the AAAA and AAAB type compounds of series **11**; without an excess of A then other products such as the AABB and AABB isomers, *e.g.* **12**, can also be formed. Examples of experimental conditions are given in the Experimental section and characterization data for particular AAAB products are provided in Table 4. All reactions yield the AAAA compound, the octakis(alkyl)phthalocyanine, as a side-product.

2,3-DICYANOHYDROQUINONE — A PRECURSOR TO TRI- AND TETRA-SUBSTITUTED PHTHALONITRILES

A further application of 2,3-dicyanohydroquinone exploits the conversion of the compound into the mono- and di-bromo substituted derivative using *N*-bromosuccinimide [47], Fig. 8. Attempts to alkylate the phenolic OH groups using a conventional Williamson's ether synthesis unexpectedly gave only the monobrominated material. However, 4,5-dibromo-3,6-dibutoxy phthalonitrile was obtained using the Mitsunobu reaction. Both compounds are well-suited for further cross-coupling reactions to replace bromide by other functionality denoted in Fig. 8 as Z. A published example of this is illustrated in Fig. 9 [48]. Further applications of this chemistry will be published in a forthcoming paper.

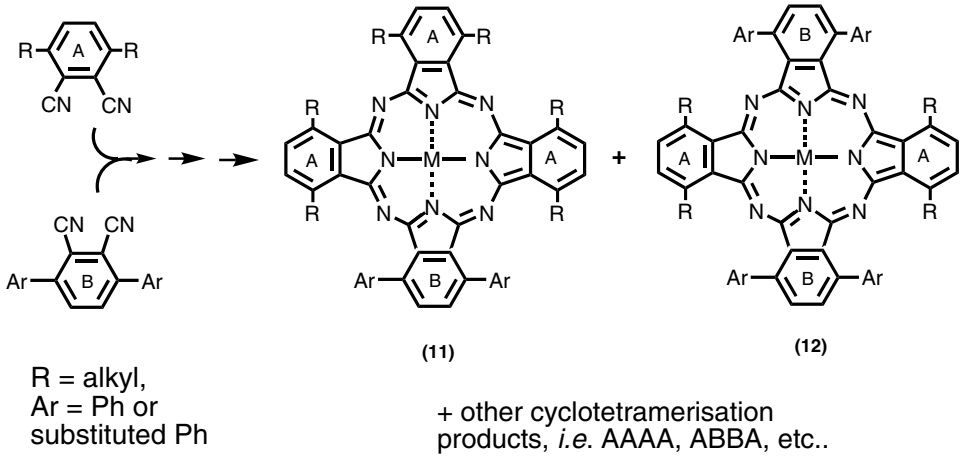


Fig. 7. Scheme to prepare cross-condensation products from a 3,6-dialkylphthalonitrile and a 3,6-diarylphthalonitrile. Novel examples of series **11** and **12** showing substituents, M, and characterization data are collected in Table 4

Table 4. Characterization data for examples of novel hexakis(alkyl) diaryl substituted phthalocyanines, series **11**

#	1,4,8,11, 15,18-groups	22,25-groups	M	Yield, %	mp	Formula and CHN Found & (Required) C H N	^{1}H NMR spectral data, $CDCl_3$ solvent unless stated otherwise; δ, ppm	λ_{max}, nm ($\varepsilon \times 10^{-5}$) THF
11a	decyl	phenyl	Zn	4[a]	> 250	$C_{104}H_{144}N_8Zn$ 79.43 9.37 6.84 (79.54 9.25 7.14)	Measured in d_6-benzene: 8.20 (d, 4H, *J*7.5), 7.89 (s, 2H), 7.87 (s, 2H), 7.81 (m, 4H), 7.61 (t, 4H, *J*5.5), 7.54 (d, 2H, *J*7.5), 4.63 (t, 4H, *J*7), 4.58 (t, 4H, *J*7), 3.41 (t, 4H, *J*7), 2.37 (m, 8H), 1.11–1.77 (m, 106H)	723 (1.55)
11b	decyl	4-MeOPh	Zn	9	> 250	$C_{106}H_{148}N_8O_2Zn$ 77.87 9.12 6.59 (78.02 9.14 6.87)	7.94 (s, 2H), 7.93 (d, 4H, *J*8.1), 7.74 (d, 2H, *J*7.5), 7.62 (d, 2H, *J*7.5), 7.45 (s, 2H), 7.11 (d, 4H, *J*8.1), 4.35 (t, 4H, *J*8), 4.22 (t, 4H, *J*8), 3.96 (s, 6H), 3.19 (t, 4H, *J*8), 2.08 (m, 4H), 1.95 (m, 4H), 0.71–1.45 (m, 106H)	713 (1.40)
11c	decyl	3-MeOPh	Zn	8	> 250	$C_{106}H_{148}N_8O_2Zn$ 77.91 9.37 6.10 (78.02 9.14 6.87)	Measured in $CDCl_3$ + 1 drop d_5-pyridine: 7.88 (s, 2H), 7.77 (s, 2H), 7.68 (d, 2H, *J*7.6), 7.48 (dd, 4H, *J*8.2, 7.6), 7.30 (dd, 2H, *J*8.2, 7.6), 7.07 (brs, 2H), 6.63 (brs, 2H), 4.53 (m, 8H), 3.83 (s, 6H), 3.24 (t, 4H, *J*8), 2.16 (m, 8H), 0.71–1.60 (m, 106H)	7.14 (1.55)
11d	pentyl	4-MeOPh	Zn	17	> 250	$C_{76}H_{88}N_8O_2Zn$ 75.29 7.54 8.68 (75.38 7.32 9.25)	7.95 (s, 2H), 7.94 (d, 4H, *J*8.5), 7.79 (s, 2H), 7.78 (d, 2H, *J*7.5), 7.65 (d, 2H, *J*7.5), 7.16 (d, 4H, *J*8.5), 4.45 (m, 8H), 4.02 (s, 6H), 3.21 (t, 4H, *J*8), 2.14 (m, 8H), 1.63–0.63 (m, 46H)	711 (2.33)
11e	decyl	3-MeOPh	H,H	10	> 250	$C_{106}H_{148}N_8O_2H_2$ 81.17 9.61 6.83 (81.18 9.64 7.14)	7.95 (s, 2H), 7.84-7.80 (m, 4H), 7.69 (d, 2H, *J*7.3), 7.55 (m, 2H), 7.49 (d, 4H, *J*7.5), 7.15 (m, 2H), 4.39 (m, 8H), 3.84 (s, 6H), 3.16 (t, 4H, *J*8), 2.10 (m, 8H), 1.01–0.72 (m, 106H), 0.32 (s, 2H)	725 (1.95)
11f	pentyl	3-MeOPh	H,H	4	> 250	$C_{76}H_{88}N_8O_2H_2$ 79.39 7.80 9.42 (79.54 7.90 9.76)	7.96 (s, 2H), 7.84 (d, 2H, *J*7.2), 7.82 (s, 2H),7.71 (d, 2H, *J*7.2), 7.56 (m, 2H), 7.50 (d, 4H, *J*6.9), 7.17 (m, 2H), 4.41 (t, 8H, *J*7.2), 3.85 (s, 6H), 3.17 (t, 4H, *J*7.2), 2.08 (q, 8H), 1.55–1.05 (m, 28H), 0.87 (m, 12H), 0.68 (t, 6H, *J* 6.6), 0.33 (s, 2H)	722 (1.73)

[a] An example of a compound of type **12** was also obtained. See the Experimental section.

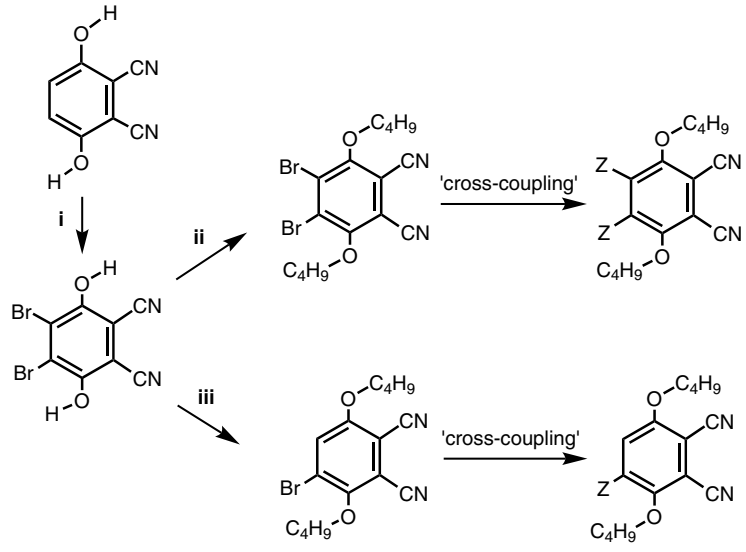


Fig. 8. Scheme showing the conversion of 2,3-dicyanohydroquinone into 4,5-dibromo-2,3-dicyanohydroquinone and products of butylation of the latter under different conditions. (i) *N*-bromosuccinimide; (ii) DIAD/PPh_3/butanol; (iii) K_2CO_3/iodobutane

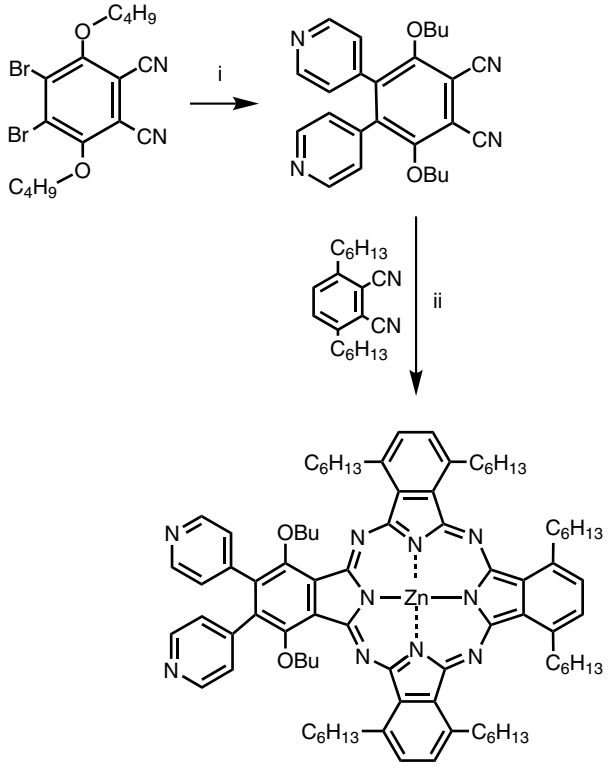


Fig. 9. Suzuki coupling. (i) pyridine boronic acid, $Pd(PPh_3)_4$, CsF in DME; (ii) $Zn(OAc)_2$ in Li/BuOH under reflux to form the AAAB type cyclotetramerisation product [48]

EXPERIMENTAL

Equipment

^{1}H NMR spectra were measured in $CDCl_3$ at 270 MHz on a Jeol EX 270 or at 300 MHz on a Varian Gemini-300 using TMS as the internal reference. Mass spectra were obtained using the MALDI technique in Dithranol matrix or the FAB technique in Noba matrix. UV/vis. spectra were measured using a Hitachi U-3000 spectrophotometer. Elemental analyses for C, H and N were undertaken by the analytical groups at either UEA or London Metropolitan University.

Compounds

3,6-Bis(trifluoromethanesulfonyloxy)-phthalonitrile. Trifluoromethanesulfonic anhydride (22.1 g, 0.078 mol) in a solution of dry DCM (10 mL) was added dropwise to a cooled solution (-20 °C) of 2,3-dicyanohydroquinone in DCM (30 mL) and dried 2,6-lutidine (16 mL). The reaction mixture was allowed to warm to rt with stirring over 14 h under argon. DCM was removed under reduced pressure and ethyl acetate (50 mL) was added. The resulting solution was washed sequentially with 5% HCl (2 × 20 mL), 5% aq. NaOH solution (2 × 20 mL) and brine (20 mL) and then dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was recrystallized (ethyl acetate/cyclohexane) to afford the *title compound* (12.71 g, 92%) as a pale yellow crystalline solid (mp 109–111 °C). Anal. calcd. for $C_{10}H_2N_2O_6S_2F_6$: C, 28.31; H, 0.48; N, 6.60%. Found C, 28.46; H, 0.29; N, 6.50%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.87 (s, 2H). MS (EI): *m/z* 423.9 (5.81%, $[M]^+$).

General procedure for preparing 3,6-bis(alkylsulfanyl)phthalonitriles (series 2) and 3,6-bis(arylsulfanyl)phthalonitriles (series 3)

3,6-Bis(decylsulfanyl)phthalonitrile, 2e. In a typical reaction, 3,6-bis(trifluoromethanesulfonyloxy)-phthalonitrile (2.0 g, 4.7 mmol) was added in portions

over 2 h to a stirred solution of decanethiol (3.30 g, 19.0 mmol) in dry DMF containing finely crushed potassium carbonate (2.3 g). The reaction was stirred over 72 h. The reaction mixture was poured into 5% aq. NaOH (150 mL), filtered and the mother liquor extracted with ethyl acetate (3 × 50 mL). The combined solution was washed sequentially with 5% aq. NaOH solution (50 mL), 5% HCl (50 mL) and brine (520 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting residue was recrystallised (DCM/ethyl acetate) to afford *3,6-bis(decylsulfanyl)phthalonitrile* (1.5 g, 68%) as yellow needles. Anal. calcd. for $C_{28}H_{44}N_2S_2$: C, 71.14; H, 9.39; N, 5.93%. Found C, 71.31; H, 9.38; N, 5.85%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.50 (s, 2H), 3.02 (t, 4H, *J* 7.5 Hz), 1.68 (m, 4H), 1.47–1.25 (m, 28H), 0.88 (t, 6H, *J* 6.7 Hz).

For characterization data and yields for homologs of series **2** and arylsulfanyl analogs of series **3**, see Tables 1 and 2 respectively.

General procedure for preparing 3,6-dialkylphthalonitriles, series 5, by Negishi coupling

3,6-Didecylphthalonitrile, 5i. In a typical experiment, *n*-BuLi (0.2 mL, 20 mol% in hexanes) was added at rt under argon to a mixture of dry THF (5 mL), bis(triphenylphosphine)-Ni(II)Cl_2 (0.154 g, 10 mol%) and triphenylphosphine (0.124 g, 20 mol%) to afford a blood-red slurry. 3,6-bis(trifluoromethanesulfonyloxy)-phthalonitrile (1.0 g, 2.36 mmol) was added under a fast stream of argon. The resulting pale brown solution was cooled to -78 °C. Decylzinc iodide (7.0 mmol, 5.6 mL of a 1.24 M solution) containing LiCl (0.30 g 7.0 mmol) was added via syringe and the solution warmed to rt over *ca*. 1 h. The reaction was then stirred for 16 h. 5% HCl (10 mL) was added carefully followed by ethyl acetate (20 mL). The organic layer was separated and washed with 5% HCl (10 mL) and brine (10 mL). The aqueous waste was extracted with ethyl acetate (10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated to dryness. In one work-up the crude product was stirred with acetonitrile (10 mL) for 10 min and pure 3,6-didecylphthalonitrile collected by filtration (0.67 g 70%). Alternatively the crude mixture was chromatographed (silica, DCM/hexane 3:2 as eluent) to yield the product in 63% yield (mp 70–71 °C (Lit. [8] 70 °C)).

The following were prepared similarly:

3,6-Dipentylphthalonitrile, 5a. Using the same conditions and ratios of substrate, reagent (*n*-pentylzinc iodide) and catalyst as above, the *title compound* was obtained in 56% yield as an oil. ^{1}H NMR ($CDCl_3$): δ, ppm 7.76 (s, 2H), 2.80 (t, 4H, *J* = 7.7Hz), 1.61 (m, 4H), 1.30–1.22 (m, 8H), 0.89 (t, 6H, *J* = 6.8 Hz). IR (neat): ν, cm^{-1} 3134, 2229 (CN).

3,6-Dihexylphthalonitrile, 5e. Using the same conditions and ratios of substrate, reagent (hexylzinc iodide) and catalyst as above, the *title compound* was obtained in 68% yield (mp 41–42 °C (Lit. [8] 43–44 °C)).

3,6-Bis(1,1-H-2,2-H-perfluorodecyl)phthalonitrile, 5k. Using the same conditions and ratios of substrate, reagent (1,1-H-2,2-H-perfluorodecylzinc iodide) and catalyst as above the crude product was recrystallized from α.α.α–trifluorotoluene to afford the *title compound* in 58% yield. Anal. calcd. for $C_{28}H_{10}N_2F_{34}$: C, 32.96; H, 1.06; N, 2.75%. Found C, 33.01; H, 0.82; N, 2.93%. ^{1}H NMR (C_6F_6:C_6D_6, 9:1): δ, ppm 7.36 (s, 2H), 3.16 (t, 4H, *J* = 7.9 Hz), 2.57–2.41 (m, 4H).

3,6-Bis(4-pivaloylbutyl)phthalonitrile, 5l. Using the same conditions and ratios of substrate, reagent (4-pivaloylbutylzinc iodide) and catalyst as above, the *title compound* was obtained in 62% yield as a colorless oil. Anal. calcd. for $C_{26}H_{36}N_2O_4$: C, 70.88; H, 8.24; N, 6.36%. Found C, 70.87; H, 8.21; N, 6.28%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.49 (s, 2H), 4.10 (t, 4H, *J* = 7.7 Hz), 2.91 (t, 4H, *J* = 7.2 Hz), 1.78–1.61 (m, 8H), 1.20 (s, 18H). MS (EI): *m/z* 440.1 ($[M]^+$).

3,6-Bis(6-chlorohexyl)phthalonitrile, 5m. Using the same conditions and ratios of substrate, reagent (6-chlorohexylzinc bromide) and catalyst as above, the *title compound* was obtained in 61% yield (mp 44.5–45.5 °C).

Use of Suzuki coupling protocol

3,6-Didecylphthalonitrile, 5i. BH_3 in THF (1.2 mmol, 1.2 mL of 1 M solution) was added dropwise under argon to a solution of 1-decene (0.51 g, 3.64 mmol) in dry THF (5 mL) at 0 °C. The reaction mixture was stirred for 4 h at 0 °C. Dry THF (4 mL) and anhydrous potassium phosphate (0.85 g, 4 mmol) were added and the reaction stirred for 1 h at rt. Anhydrous LiCl (0.08 g, 1.9 mmol) and 3,6-bis(trifluoromethanesulfonyloxy)phthalonitrile (0.25 g, 0.59 mmol) were added followed, after 10 min, by Pd(dppf)Cl_2 {[(1,1′-bis(diphenylphosphino)ferrocene]-dichloropalladium(II)} (21 mg, 5 mol%). The reaction mixture was heated under reflux for 10 h, cooled, filtered and the filtrate evaporated to dryness and chromatographed over silica (eluent: toluene) to afford the *title compound* (0.09 g) in 38% yield.

General procedure for preparing 3,6-diarylphthalonitriles, series 6, by cross-coupling reactions

3,6-Diphenylphthalonitrile, 6a (Suzuki coupling). In a typical experiment, 3,6-bis(trifluoromethanesulfonyloxy)-phthalonitrile (0.5 g, 1.18 mmol) and anhydrous LiCl (0.13 g, 3 mmol) were stirred in dry toluene under argon for 30 min. Tetrakis(triphenylphosphine) palladium (0) (84.0 mg, 10 mol%) was added and the mixture stirred for 10 min. Phenylboronic acid (0.43 g, 3.5 mmol) was added followed by aq. 2 M Cs_2CO_3 (2 mL). The reaction mixture was heated under reflux

for 14 h, cooled and diluted with ethyl acetate (15 mL). The mixture was washed sequentially with 10% aq. KOH solution (2 × 10 mL), 5% HCl (10 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated under reduced pressure. Recrystallization of the crude product from toluene afforded the *title compound* (0.26 g, 79%) (mp 221–223.5 °C (Lit. [31] 220 °C)).

3,6-Bis(4-*t*-butylphenyl)phthalonitrile, 6b (Suzuki coupling). Application of the Suzuki coupling conditions using 4-*t*-butylphenylboronic acid afforded the *title compound* as a colourless crystalline solid in 36% yield (mp 153 °C). Anal. calcd. for $C_{28}H_{28}N_2$: C, 85.67; H, 7.19; N, 7.14%. Found C, 85.27; H, 7.05; N, 6.74%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.77 (s, 2H), 7.55 (m, 8H), 1.38 (s, 18H). MS (EI): *m/z* 392 ([M]$^+$, 66%), 377 ([M$^+$- CH_3], 100%).

3,6-Bis(4-methoxydiphenyl)phthalonitrile, 6c (Suzuki coupling). Under the conditions used above 4-methoxyphenylboronic acid (0.45 g, 3.5 mmol) was crossed-coupled to 3,6-bis(trifluoromethanesulfonyloxy)-phthalonitrile to afford the *title compound* as a white crystalline solid (0.29 g, 73%) (mp 213–215 °C). Anal. calcd. for $C_{22}H_{16}N_2O_2$: C, 77.6; H, 4.74; N, 8.23%. Found C, 77.38; H, 4.68; N, 8.21%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.74 (s, 2H), 7.55 (d, 4H, *J* = 8.5 Hz), 7.06 (d, 4H, *J* = 8.5), 3.89 (s, 6H). MS (EI): *m/z* 340 ([M]$^+$, 21%).

3,6-Bis(4-methoxyphenyl)phthalonitrile, 6c (Negishi coupling). Application of the Negishi coupling conditions (see earlier) afforded the *title compound*, identical to the above sample, in 67% yield.

3,6-Bis(3-methoxyphenyl)phthalonitrile, 6d (Suzuki coupling). Under the conditions used above 3-methoxyphenylboronic acid (0.45 g, 3.5 mmol) was crossed-coupled to 3,6-bis(trifluoromethanesulfonyloxy)-phthalonitrile to afford the *title compound* as a white crystalline solid (0.28 g, 70%) (mp 236–239 °C). Anal. calcd. for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%. Found C, 77.54; H, 4.64; N, 8.24%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.79 (s, 2H), 7.45 (t, 2H, *J* = 8 Hz), 7.16 (ddd, 2H), 7.11 (t, 2H, *J* = 2.5 and 1.6 Hz), 7.06 (ddd, 2H), 3.89 (s, 6H). MS (EI): *m/z* 340 ([M]$^+$, 100%).

3,6-Bis(3-methoxyphenyl)phthalonitrile, 6d (Negishi coupling). Application of the Negishi coupling conditions (see earlier) afforded the *title compound*, identical to the above sample, in 67% yield.

3,6-Bis(2-methoxyphenyl)phthalonitrile, 6e (Suzuki coupling). Under the conditions used above 2-methoxyphenylboronic acid was crossed-coupled to 3,6-bis(trifluoromethanesulfonyloxy)phthalonitrile to afford the *title compound* as a pale yellow crystalline solid in 20% yield (mp 196–199 °C). Anal. calcd. for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%. Found C, 77.27; H, 4.68; N, 8.25%. ^{1}H NMR ($CDCl_3$): δ, ppm 7.54 (s, 2H), 7.30 (d, 2H, *J* = 8 Hz), 7.16 (t, 2H, *J* = 7.5 Hz), 6.96 (m, 4H), 3.71 (s, 6H). MS (EI): *m/z* 340 ([M]$^+$, 100%).

3,6-Bis(2-methoxyphenyl)phthalonitrile, 6e (Negishi coupling). Application of the Negishi coupling conditions (see earlier) afforded the *title compound*, identical to the above sample, in 30% yield.

PHTHALOCYANINE SYNTHESIS

General method for preparing zinc and magnesium metalated 1,4,8,11,15,18,22,25-octakis(alkylsulfanyl)phthalocyanines, series 8, and 1,4,8,11,15,18,22,25-octakis(arylsulfanyl)-phthalocyanines, series 9

1,4,8,11,15,18,22,25-Octakis(decylsulfanyl)-phthalocyaninato zinc, 8k. In a typical reaction, a solution of 3,6-bis(decylsulfanyl)phthalonitrile **2e** (1.01 g, 2.14 mmol) was heated in dry pentanol (9 mL) under nitrogen. DBU (0.23 g, 1.50 mmol) was added and heating continued for 1 h. Zinc acetate dihydrate (99.999% zinc, 0.14 g, 0.64 mmol) was added and the reaction heated for a further 20 h. The reaction mixture was cooled and the solvent removed under reduced pressure. The residue was chromatographed over silica (eluent: DCM/Et_3N 100:1). The first reddish-brown fraction was collected, evaporated and triturated (hot acetone) and recrystallised from THF/methanol to afford *1,4,8,11,15,18,22,25-octakis(decylsulfanyl)phthalocyaninato zinc* (0.68 g, 65%). Anal. calcd. for $C_{112}H_{176}N_8S_8Zn$: C, 68.76; H, 9.07; N, 5.73%. Found C, 69.01; H, 9.05; N, 5.71%. MS (MALDI): isotopic cluster at *m/z* 1956 ([M]$^+$). ^{1}H NMR (C_6D_6 with 1% d_5-pyridine): δ, ppm 7.86 (s, 8H), 3.38 (t, 16H, *J* = 7.25 Hz), 2.11–2.01 (m, 16H), 1.68–1.58 (m, 16H), 1.52–1.18 (m, 96H), 0.90 (t, 24H, *J* = 6.6 Hz). UV-vis (THF): λ, nm 781.

Yields and selected characterization data for zinc metalated homologs **8a**, **8f**, **8g**, **8i** and **8m** and for **9a** and **9d** are shown in Tables 1 and 2 respectively. Magnesium metalated compounds, **8b**, **8h**, **8j** and **8l**, were prepared similarly using $MgCl_2$ in place of zinc acetate. Selected characterization data and yields are also shown in Table 1.

General method for preparing lead, chloroindium and copper metalated 1,4,8,11,15,18,22,25-octakis-(alkylsulfanyl or arylsulfanyl)phthalocyanines of series 8 and 9

1,4,8,11,15,18,22,25-Octakis(hexylsulfanyl)-phthalocyaninato lead, 8c. By adapting the general method above, the *title compound* was prepared from 3,6-bis(hexylsulfanyl)phthalonitrile (0.5 g, 1.39 mmol) in pentanol (7 mL), in the presence of DBU (0.14 mL, 0.097 mmol) and lead acetate (0.15 g, 0.42 mmol). The compound was purified by chromatography over silica, pre-treated with DCM:Et_3N 99:1, using DCM as eluent, and recrystallized from THF/acetone to give the *title compound* (87 mg, 15%) as dark red crystals (mp 145–148 °C). MS (MALDI): isotopic cluster at *m/z* 1650 ([M

+ 1]$^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 1.

1,4,8,11,15,18,22,25-Octakis(phenylsulfanyl)-phthalocyaninato lead, **9b**, and **1,4,8,11,15,18,22,25-octakis(4-methylphenylsulfanyl)phthalocyaninato lead**, **9e**, were prepared similarly, see Table 2.

1,4,8,11,15,18,22,25-Octakis(hexylsulfanyl)-phthalocyaninato chloroindium, 8d. Application of the method above gave the *title compound* from 3,6-bis(hexylsulfanyl)phthalonitrile (0.5 g, 1.39 mmol) in pentanol (7 mL), in the presence of DBU (0.14 mL, 0.097 mmol) and indium(III) chloride (93 mg, 0.42 mmol). The compound was purified by chromatography over silica, pre-treated as above with DCM:Et_3N 99:1. A first (yellow) fraction was eluted with DCM and discarded. Change of eluent to THF gave a dark second fraction. This was re-chromatographed using first DCM and then DCM:THF (95:5) collecting the first deep blue fraction. The recrystallized (THF/acetone) sample of the *title compound* (17 mg, 3%) was obtained as a deep blue/black solid (mp 202–204 °C). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 1.

1,4,8,11,15,18,22,25-Octakis(4-methylphenylsulfanyl)phthalocyaninato chloroindium, **9c**, and **1,4,8,11,15,18,22,25-octakis(4-methylphenylsulfanyl)-phthalocyaninato chloroindium**, **9f**, were prepared similarly, see Table 2.

1,4,8,11,15,18,22,25-Octakis(hexylsulfanyl)-phthalocyaninato copper, 9e. Adapting the general method above, the *title compound* was obtained from 3,6-bis(hexylsulfanyl)phthalonitrile (0.5 g, 1.39 mmol) in pentanol (7 mL), in the presence of DBU (0.14 mL, 0.097 mmol) and copper acetate (84 mg, 0.42 mmol). The product was chromatographed over silica, eluent DCM:Et_3N 99:1, and the *title compound* collected as the first colored fraction and recrystallized from THF/acetone (289 mg, 55%) (mp 135–140 °C). MS (MALDI): isotopic cluster at *m/z* 1607 ([M]$^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 1.

Bis[1,4,8,11,15,18,22,25-octakis(4-t-butylphenylsulfanyl)phthalocyaninato] cerium(IV), 10, and 1,4,8,-11,15,18,22,25-octakis(4-t-butylphenylsulfanyl)-phthalocyanine, 9g. Application of the method above gave both *title compounds* from 3,6-bis(4-*t*-butylphenylsulfanyl)-phthalonitrile (1.00 g, 2.20 mmol) in pentanol (20 mL) in the presence of DBU (1.33 g, 8.77 mmol) and cerium(III) chloride (32 mg, 0.13 mmol) and after heating under reflux for 5 h. The compound mixture was separated by chromatography over silica, eluent DCM, to give *1,4,8,11,15,18,22,25-octakis(4-t-butylphenylsulfanyl)-phthalocyanine* as the first fraction (100 mg, 10%) as a dark red crystalline solid (mp 155–156 °C). MS (MALDI): isotopic cluster at *m/z* 1827.5 ([M]$^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 2. The second fraction eluted with DCM/THF (9:1) afforded *bis[1,4,8,11,15,18,22,25-octakis(4-t-butylphenylsulfanyl)-phthalocyaninato cerium(IV)* as a purple solid (mp 196–197 °C). MS (MALDI): isotopic cluster at *m/z* 3792.3 ([M]$^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 2.

General method for preparing 1,4,8,11,15,18-hexakis(alkyl)-22,25-bis(aryl)-phthalocyaninato zinc derivatives

1,4,8,11,15,18-Hexakis(decyl)-22,25-bis(phenyl)-phthalocyaninato zinc, 11a, (and compound 12). DBU (106 mg) was added to a refluxing solution of 3,6-diphenylphthalonitrile (0.28 g, 1.00 mmol) and 3,6-didecylphthalonitrile (0.82 g, 2.00 mmol) in pentanol (10 mL). Heating under reflux was continued for 1 h, zinc acetate dihydrate (0.07 g, 0.3 eq.) was added, and the solution was heated under reflux for a further 24 h. Removal of solvent and trituration of the resultant slurry with methanol afforded a green solid that was chromatographed over silica. The first fraction collected (eluent petrol/DCM 9:1) was 1,4,8,11,15,18,22,25-octakis(decyl)phthalocyaninato zinc (105 mg, 7%), identical with an authentic sample [49]. Further elution (petrol/DCM 9:1) afforded *1,4,8,11,15,18-hexakis(decyl)-22,25-bis(phenyl)phthalocyaninato zinc* **11a** (60 mg, 4%) after recrystallization from THF/MeOH (mp > 250 °C). MS (MALDI): isotopic cluster at *m/z* 1571 ([M]$^+$). Further characterization data are collected in Table 3. Changing the eluent (petrol/DCM 1:3) afforded a third fraction *1,4,15,18-tetrakis(decyl)-8,11,22,25-tetrakis(phenyl) phthalocyaninato zinc* **12** (30 mg, 2%) as a green solid (mp > 250 °C). MS (MALDI): isotopic cluster at *m/z* 1443 ([M]$^+$). ^{1}H NMR (C_6D_6): δ, ppm 7.76 (s, 4H), 7.73 (d, 4H, J = 7.7 Hz), 7.70 (s, 4H), 7.67 (d, 8H, J = 7.7 Hz), 7.42 (t, 8H, J = 7.7 Hz), 3.49 (t, 8H, J = 7.5 Hz), 1.76 (m, 8H), 1.36–1.05 (m, 56H), 0.81 (t, 12H, J = 7.5 Hz). UV-vis (THF): λ, nm 723 (ε 1.55×10^5).

1,4,8,11,15,18-Hexakis(decyl)-22,25-bis(4-methoxyphenyl)phthalocyaninato zinc, 11b. Applying the method described above, 3,6-bis(4-methoxyphenyl)-phthalonitrile (0.13 g, 0.38 mmol), 3,6-didecylphthalonitrile (0.94 g, 2.29 mmol), DBU (30 mg, 0.7 eq.) and zinc acetate dihydrate (0.18 g, 0.3 eq.) in pentanol (10 mL) afforded *1,4,8,11,15,18-hexakis(decyl)-22,25-bis(4-methoxyphenyl)phthalocyaninato zinc* (50 mg, 8%) as the second fraction during separation over silica (petrol/DCM) (mp > 250 °C). MS (MALDI): isotopic cluster at *m/z* 1631 ([M]$^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 4.

1,4,8,11,15,18-Hexakis(decyl)-22,25-bis(3-methoxyphenyl)phthalocyaninato zinc, 11c. Applying the method described above, 3,6-bis(3-methoxyphenyl)-phthalonitrile (0.13 g, 0.38 mmol), 3,6-didecylphthalonitrile (0.94 g, 2.29 mmol), DBU (30 mg, 0.7 eq.) and zinc acetate dihydrate (0.18 g, 0.3 eq.) in pentanol (10 mL) afforded

1,4,8,11,15,18-hexakis(decyl)-22,25-bis(3-methoxyphenyl)phthalocyaninato zinc (50 mg, 8%) as the second fraction during separation over silica (petrol/DCM) (mp >250 °C). MS (MALDI): isotopic cluster at *m/z* 1631 ($[M]^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 4.

1,4,8,11,15,18-Hexakis(pentyl)-22,25-bis(4-methoxyphenyl)phthalocyaninato zinc, 11d. Applying the procedure described above, 3,6-bis(3-methoxyphenyl)-phthalonitrile (0.41 g), 3,6-dipentylphthalonitrile (1.60 g), DBU (265 mg) and zinc acetate dihydrate (175 mg) in pentanol (15 mL) afforded *1,4,8,11,15,18-hexakis(pentyl)-22,25-bis(3-methoxyphenyl)phthalocyaninato zinc* (210 mg, 17%) as the second fraction during separation over silica (petrol/DCM) (mp > 250 °C). MS (MALDI): isotopic cluster at *m/z* 1211 ($[M]^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 4.

General method for preparing 1,4,8,11,15,18-hexakis(alkyl)-22,25-bis(aryl)-phthalocyanines

1,4,8,11,15,18-Hexakis(decyl)-22,25-bis(3-methoxyphenyl)phthalocyanine, 11e. Lithium metal (0.40 g) was added portionwise to a solution of 3,6-bis(3-methoxyphenyl)phthalonitrile (0.33 g, 0.97 mmol) and 3,6-didecylphthalonitrile (3.57 g, 8.73 mmol) in pentanol (30 mL) heated under reflux for 6 h. Glacial acetic acid (40 mL) was added to the cooled solution and the mixture stirred for 1 h. The solvents were removed under reduced pressure and the resultant slurry triturated with methanol. The green solid was collected and chromatographed over silica. The first fraction (eluent: petrol/DCM 9:1) was collected and shown to be 1,4,8,11,15,18,22,25-octakis(decyl)phthalocyanine (0.98 g, 28%), identical to an authentic sample. The second fraction eluted with petrol/DCM 7:3, *1,4,8,11,15,18-hexakis(decyl)-22,25-bis(3-methoxyphenyl)phthalocyanine* (152 mg, 10%) was recrystallized from THF/MeOH. MS (MALDI): isotopic cluster at *m/z* 1568 ($[M]^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 4.

1,4,8,11,15,18-Hexakis(pentyl)-22,25-bis(3-methoxyphenyl)phthalocyanine, 11f. Using the same procedure as above, the *title compound* (40 mg, 4%) was obtained as the second fraction from the reaction of 3,6-bis(3-methoxyphenyl)phthalonitrile (0.33 g, 0.97 mmol) and 3,6-dipentylphthalonitrile (2.34 g, 8.73 mmol) in pentanol (30 mL) into which lithium metal had been added. MS (MALDI): isotopic cluster at *m/z* 1147 ($[M]^+$). CHN analysis results, ^{1}H NMR data and Q-band λ_{max} are given in Table 4.

CONCLUSION

This review discusses synthetic routes for the syntheses of various 3,6-disubstituted phthalonitriles where the substituents are alkoxy, alkylsulfanyl, the recently described phenylselenyl, alkyl, functionalized-alkyl and aryl groups. Such compounds are immediate precursors to a wide range of 1,4,8,11,15,18,22,25-(non-peripheral) octasubstituted phthalocyanine derivatives. Early routes for the preparation of 3,6-dialkylphthalonitriles, 3,6-functionalized dialkylphthalonitriles and 3,6-diphenylphthalonitrile employed Diels–Alder chemistry within convenient but multistep sequences. However, an attractive alternative access to these and other classes of 3,6-disubstituted phthalonitriles is the use of 2,3-dicyanohydroquinone, a precursor that has the two adjacent cyano groups already in place together with two phenolic OH groups. Alkylation of the OH groups provided early access to 3,6-dialkoxyphthalonitriles and thence non-peripherally octaalkoxy substituted phthalocyanine derivatives. However, conversion of 2,3-dicyanohydroquinone to the bis-triflate derivative offers the prospect of cleaving the ring-to-oxygen bond to enable alternative functionality to be introduced. This has been illustrated through the use of S_NAr reactions to introduce alkylsulfanyl, arylsulfanyl and phenylselenyl groups at the 3,6-positions of the phthalonitrile unit. In addition the advent of organometallic catalyzed cross-coupling reactions to create new carbon-carbon bonds adds a further dimension that allows direct incorporation of alkyl and aryl substituents at the 3- and 6-positions of phthalonitrile. Finally, bromination of 2,3-dicyanohydroquinone to form 5,6-dibromo-2,3-dicyanohydroquinone is shown to provide access to both monobromo and dibromo derivatives of 3,6-dibutoxyphthalonitrile. These compounds provide opportunities for cross-coupling reactions at the brominated sites to provide more complex derivatives with the potential to serve as precursors of highly substituted phthalocyanine derivatives. Examples of a range of phthalocyanine compounds derived from the phthalonitrile precursors described above are included in the review.

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