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The synthesis of symmetrical peripheral and non-peripheral octa-substituted metal-free phthalocyanines: simpler, better, faster, cheaper

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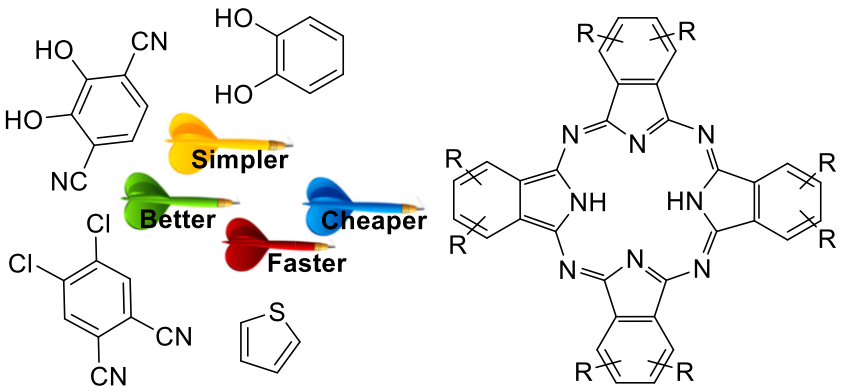
Abstract

Phthalocyanines are important not only as industrial pigments, but also in photodynamic cancer therapy, catalysis and various other fields. Despite the huge demand, synthetic routes to Pcs are tedious and the yields poor. In this paper, we report on modifications to the syntheses of symmetrical octa-substituted metal-free phthalocyanines (H_2Pc). H_2Pcs with peripheral or non-peripheral alkyl substituents were prepared in less steps and in higher yields than previously reported, whereas the yields of H_2Pcs with alkoxy substituents (peripheral or non-peripheral) were improved considerably.



Keywords: Phthalocyanine, peripheral, non-peripheral, alkyl, alkoxy, aryloxy

Introduction

With applications in dyes, photodynamic cancer therapy, photochemical and photovoltaic cells, laser printing, optical communication and catalysis,[1] phthalocyanines (Pcs) are of considerable industrial importance. The Pc pigment market alone was valued at $1.4 billion in 2019.[2]

The phthalocyanine skeleton (**1**) (Fig. 1) is a tetraazatetrabenzoporphyrin (TABP) consisting of four isoindoline units linked by four *meso* nitrogen bridges. The resulting conjugated 18 π electron system, which can host more than 95 metals/metalloids in the central cavity, is responsible for the appealing photophysical, photochemical and electrochemical properties of Pcs.[3,4] Pcs are commonly modified by (i) substituents on the peripheral (β) and/or non-peripheral (α, bay) positions, (ii) by changing the central metal/metalloid or (iii) axial ligands (depending on the oxidation state of the metal and a preference for hexa-coordination over tetra-coordination). Substituents not only have an effect on π-stacking and thus aggregation and solubility, but also on the electronic properties of the Pc.

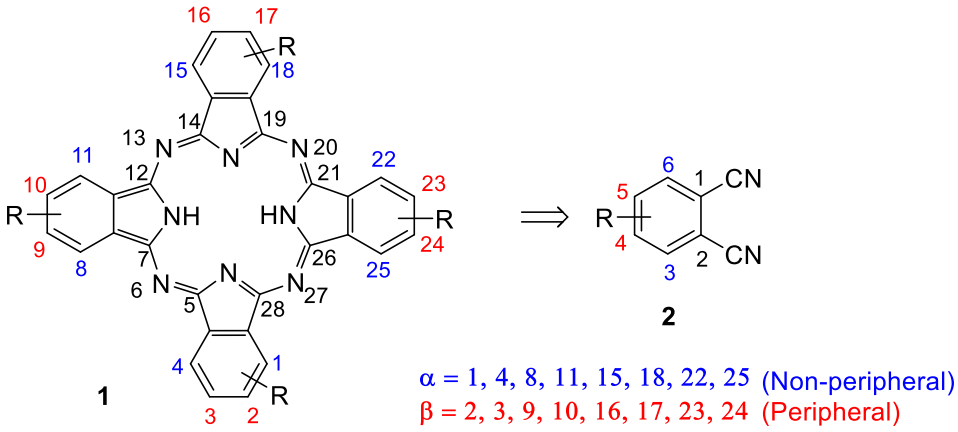


Figure 1. The metal-free phthalocyanine (H_2Pc) skeleton and retrosynthesis to phthalonitriles

Metal-free Pcs (H_2Pc) may be obtained from the corresponding phthalonitrile (1,2-dicyanobenzene)[4] (**2**) by alkali-induced cyclotetramerization according to the Tomada method,[5] reductive cyclotetramerization at elevated temperatures (>180 °C),[6] template cyclotetramerization with metal alkoxides according to the Linstead method and displacement of the metal cation by acidification,[4] or treatment with ammonia and subsequent cyclotetramerization of the 1,3-diiminoisoindoline.[7] However, despite being critical to numerous industries, synthetic routes to Pcs are elaborate and time-consuming, and the yields are often poor (*vide infra*). In this paper, we thus report on improvements to the syntheses of octa-substituted metal-free phthalocyanines (H_2Pcs). H_2Pcs with alkyl substituents in the peripheral or non-peripheral positions could be prepared in less steps and in higher yields than previously reported, whereas the yields of H_2Pcs with alkoxy substituents (peripheral or non-peripheral) could be improved considerably.

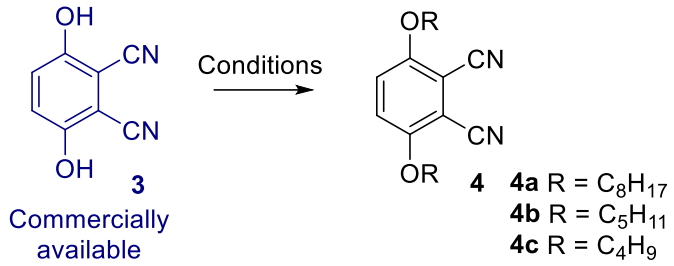
Results and Discussion

We started our investigations with improvements to the synthesis of 3,6- and 4,5-disubstituted phthalonitriles with alkyl, alkoxy and aryloxy substituents.

3,6-Dialkoxyphthalonitriles (4). Cook et al.[8] reported the preparation of 3,6-dialkoxyphthalonitriles (**4**) via the etherification of commercially available 2,3-dicyanohydroquinones (**3**) with alkyl halides in refluxing acetone and K_2CO_3 as base. Yields of ca. 50 - 60% were achieved over 2.5 days (Table 1, entries 1 – 3). As alkyl bromides are more readily available than alkyl iodides, the etherification of 2,3-

dicyanohydroquinones (**3**) was attempted with octyl bromide. 3,6-Dioctyloxyphthalonitrile (**4a**) was obtained in only 22% yield after 7 days, compared to the reported yield of 51% with the alkyl iodide (Table 1, entry 4 vs 1). It was thus decided to prepare the alkyl iodide in situ from the alkyl bromide and KI. The alkoxylation was still unacceptably slow and **4a** was obtained in only 15% yield after 4 days. In order to increase the rate of the reaction by increasing the temperature, the solvent was changed from acetone to DMF. 3,6-Dioctyloxyphthalonitrile (**4a**) could thus be obtained in quantitative yield within 24 h at 80 °C as opposed to only 22% after 7 days according to the original procedure (Table 1, entry 6 vs 4). Similar conditions also afforded the pentoxy (**4b**) and butoxy (**4c**) phthalonitrile derivatives in 83% and 84% yield, respectively (vs 58% and 50% reported by Cook et al.;[8] Table 1, entries 7 and 8 vs 2 and 3).

Table 1. Etherification of 3,6-dihydroxyphthalonitrile (**3**)



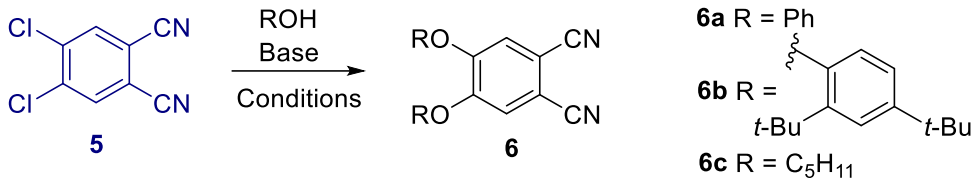
Entry	RX	RX (eq)	Solvent	K_2CO_3 (eq)	T (°C)	KI (eq)	Time (days)	Product	Yield (%)
Previous work									
1	$C_8H_{17}I$	5	Acetone	4.5	56	-	2.5	**4a**	51[8]
2	$C_5H_{11}I$	5	Acetone	4.5	56	-	2.5	**4b**	58[Error! Bookmark not defined.]
3	C_4H_9I	5	Acetone	4.5	56	-	2.5	**4c**	50[8]
This work									
4	$C_8H_{17}Br$	3	Acetone	4	56	-	7	**4a**	22
5	$C_8H_{17}Br$	3	Acetone	4	56	0.2	4	**4a**	15
6	$C_8H_{17}Br$	3	DMF	4	80	0.2	1	**4a**	99
7	$C_5H_{11}Br$	3	DMF	4	80	0.3	1	**4b**	83
8	C_4H_9Br	2.4	DMF	4	80	0.4	1	**4c**	84

Reagents and conditions: **3**, K_2CO_3, KI and RX in solvent were kept at the temperature as indicated.

With the starting materials for non-peripheral alkoxy Pcs obtained in good yields, attention was subsequently turned towards the preparation of the reactants for the peripheral alkoxy analogues.

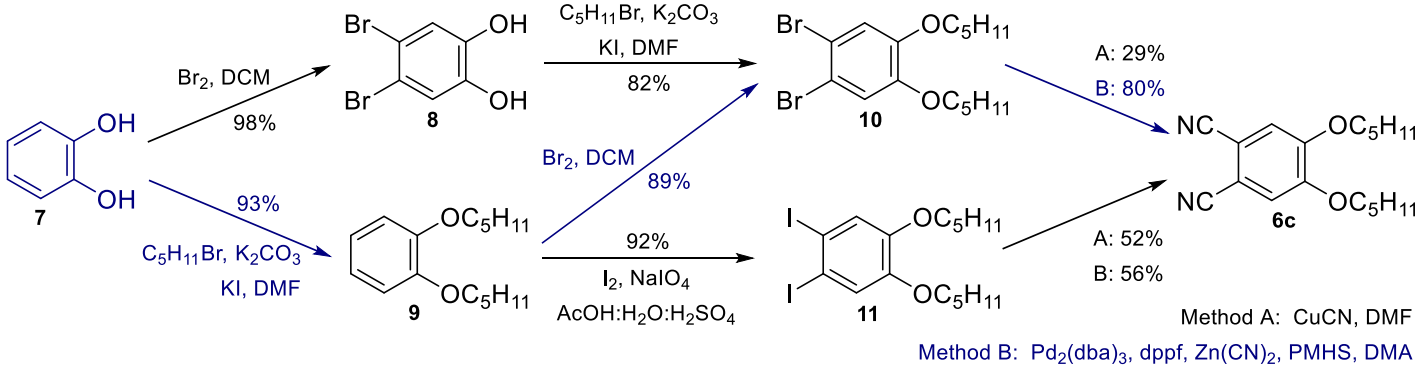
4,5-Dialkoxy- and 4,5-diaryloxyphthalonitriles (6). In a nucleophilic aromatic substitution reaction, Platonova, Volov and Tomilova[9] prepared 4,5-diaryloxyphthalocyanines from commercially available 4,5-dichlorophthalonitrile (**5**) in 65% yield and the corresponding palladium(II) octaaryloxyphthalocyanines in 20% overall yield. Bulky 2,4-di-*tert*-butylphenoxy substituents have been demonstrated to reduce aggregation of Pcs, rendering it soluble in a variety of solvents.[10] We therefore treated 4,5-dichlorophthalonitrile (**5**) with 2,4-di-*tert*-butylphenol and K_2CO_3 in DMF to obtain 4,5-bis(2,4-di-*tert*-butylphenoxy)phthalonitrile (**6b**) in 78% yield (Table 2, entry 2). S_NAr with deprotonated pentanol (NaH), however, gave the 4,5-dipentyloxyphthalonitrile (**6c**) in an unacceptable 13% yield at room temperature (Table 2, entry 3), whereas higher temperatures resulted in even lower yields.

Table 2. Nucleophilic aromatic substitution of the chloro substituents of 4,5-dichlorophthalonitrile (**5**)



Entry	ROH	ROH eq	Solvent	Base	Base (eq)	T (°C)	Time (h)	Product	Yield (%)
Previous work									
1	PhOH	6	DMSO	K_2CO_3	16	90	1-3	**6a**	65[11]
This work									
2	2,4-di-*t*-BuPhOH	2.1	DMF	K_2CO_3	7	80	12	**6b**	78
3	$C_5H_{11}OH$	2.1	DMF	NaH	2.1	0 - rt	48	**6c**	13

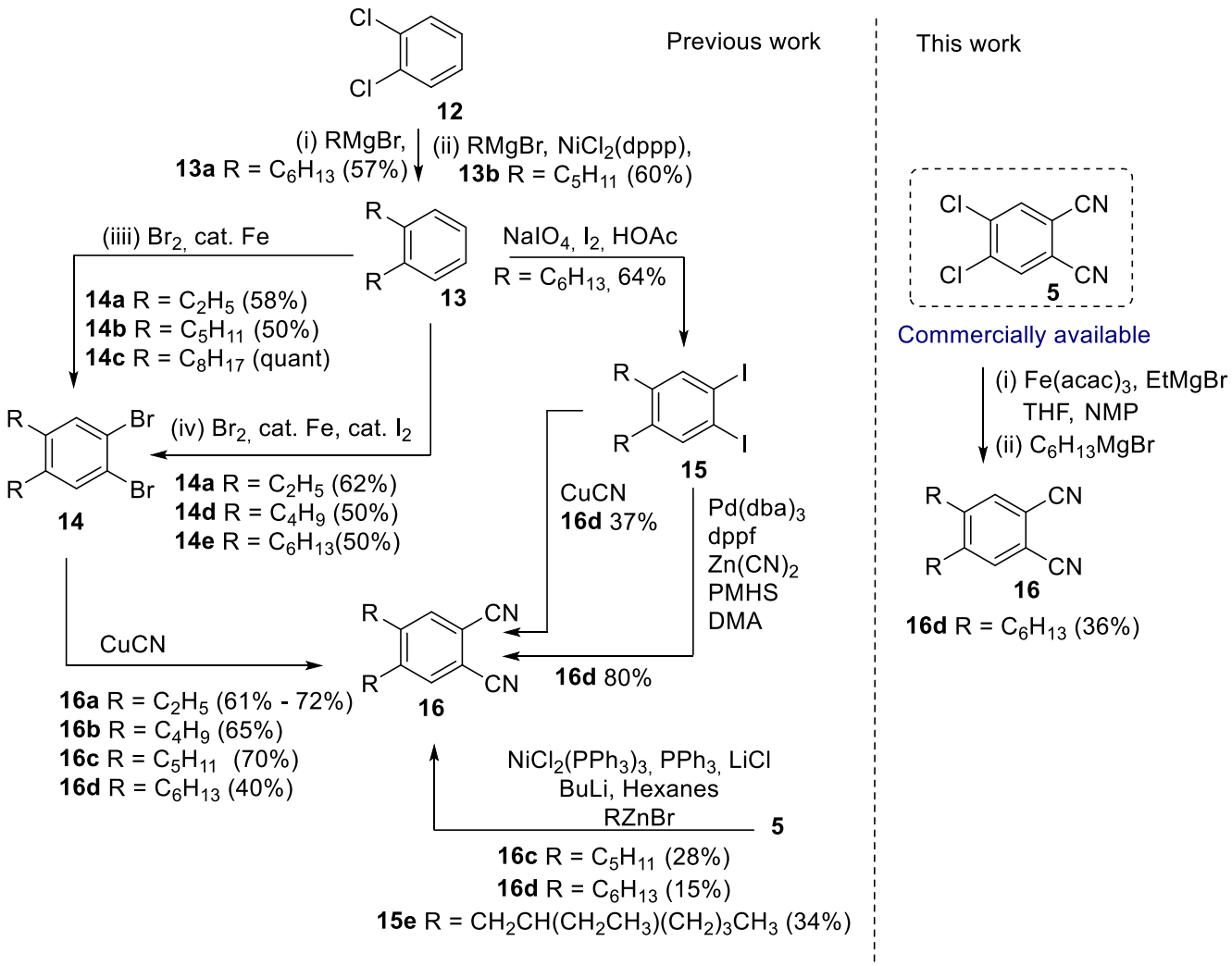
Since 4,5-dialkoxyphthalonitriles (**6**) are commonly prepared from catechol (**7**) via the intermediate 1,2-dibromo-4,5-dialkoxybenzene (**8**) following either a two-step bromination-alkylation[12] or a two-step alkylation-bromination[Error! Bookmark not defined.] sequence (Scheme 1), we subsequently opted for this approach in order to improve yields. The higher temperature achieved in DMF allowed for the synthesis of 1,2-dibromo-4,5-dipentoxybenzene (**10**) in overall yields of 80% (bromination-alkylation) and 83% (alkylation-bromination), respectively. The initial alkylation conveniently allowed for either bromination or iodination of the intermediate 1,2-dialkoxybenzene (**9**), so I_2/$NaIO_4$ iodination[13,14] gave 1,2-diiodo-4,5-dipentoxybenzene (**11**) in excellent yield (92%). Rosenmund-von Braun cyanation (CuCN, DMF, 140 °C) gave the desired 4,5-dipentoxyphthalonitrile (**6c**) in 29% and 52% yield from the dibromo- (**10**) and diiodo-4,5-dipentoxybenzenes (**11**), respectively, whereas cyanation by means of a palladium-catalyzed Negishi coupling of 1,2-dibromo-4,5-dipentoxybenzene (**10**) with $Zn(CN)_2$, according to a procedure reported by Seki,[15] gave 4,5-dipentoxyphthalonitrile (**6c**) in 80% yield. When applied to the iodo analogue (**11**), a yield of only 56% could be achieved, though.



Scheme 1. The preparation of 4,5-dialkoxyphthalonitriles (**6**) from catechol (**7**) via the intermediate 1,2-dihalo-4,5-dialkoxybenzenes (**10** and **11**). *dba = dibenzylideneacetone ; dppf = 1,1'-bis(diphenylphosphino)-ferrocene ; PMHS = polymethylhydrosiloxane ; DMA = dimethylacetamide*

4,5-Dialkylphthalonitriles (16). The classical pathway to 4,5-dialkylphthalonitriles (**16**) en route to peripheral Pc's, entails a three-step synthesis involving the Grignard reaction of 1,2-dichlorobenzene (**12**) (or the 1,2-dibromo analogue) with RMgBr or nickel catalyzed coupling of these reagents [RMgBr, $NiCl_2$(dppp)]; bromination (Br_2, cat. Fe or Br_2, cat. Fe, cat. I_2) or iodination ($NaIO_4$, I_2, HOAc) of the 1,2-dialkylbenzene (**13**); and finally Rosenmund-von Braun (CuCN, DMF) or Negishi [$Pd_2(dba)_3$, dppf, $Zn(CN)_2$, PMHS, DMA] cyanation (yields over 3 steps: ca 25 – 29%) (Scheme 2).[12,16-19]

Most convenient at this stage, is the one step Negishi cross-coupling of commercially available 4,5-dichlorophthalonitrile (**5**) with alkylzinc bromide [bis(triphenylphosphine)nickel(II)dichloride, PPh_3, LiCl, BuLi], though the yields are quite low [28% for R = pentyl (**16c**), 15% for R = hexyl (**16d**), 34% for R = 2-ethyl-1-hexyl (**16e**)] (Scheme 2).[20] Apart from requiring alkyl zinc halide reagents that are not readily available, the Negishi reaction also requires cryogenic temperatures (-78 °C) and overnight reaction times. As custom Grignard reagents may be prepared by exchange reactions with readily available Grignard reagents such as EtMgBr, we applied an iron-catalyzed Grignard reaction[21,22] to the synthesis of phthalonitriles for the first time. The yield of 4,5-dihexylphthalonitrile **16d** prepared in this way (36%), was more than double the reported yield for the corresponding Negishi reaction (15%) (Scheme 2). The appeal of this one-step method furthermore lies in the ease of execution with regard to temperature (-10 °C vs -78 °C) and the reaction being faster than the Negishi coupling (4 h vs overnight).



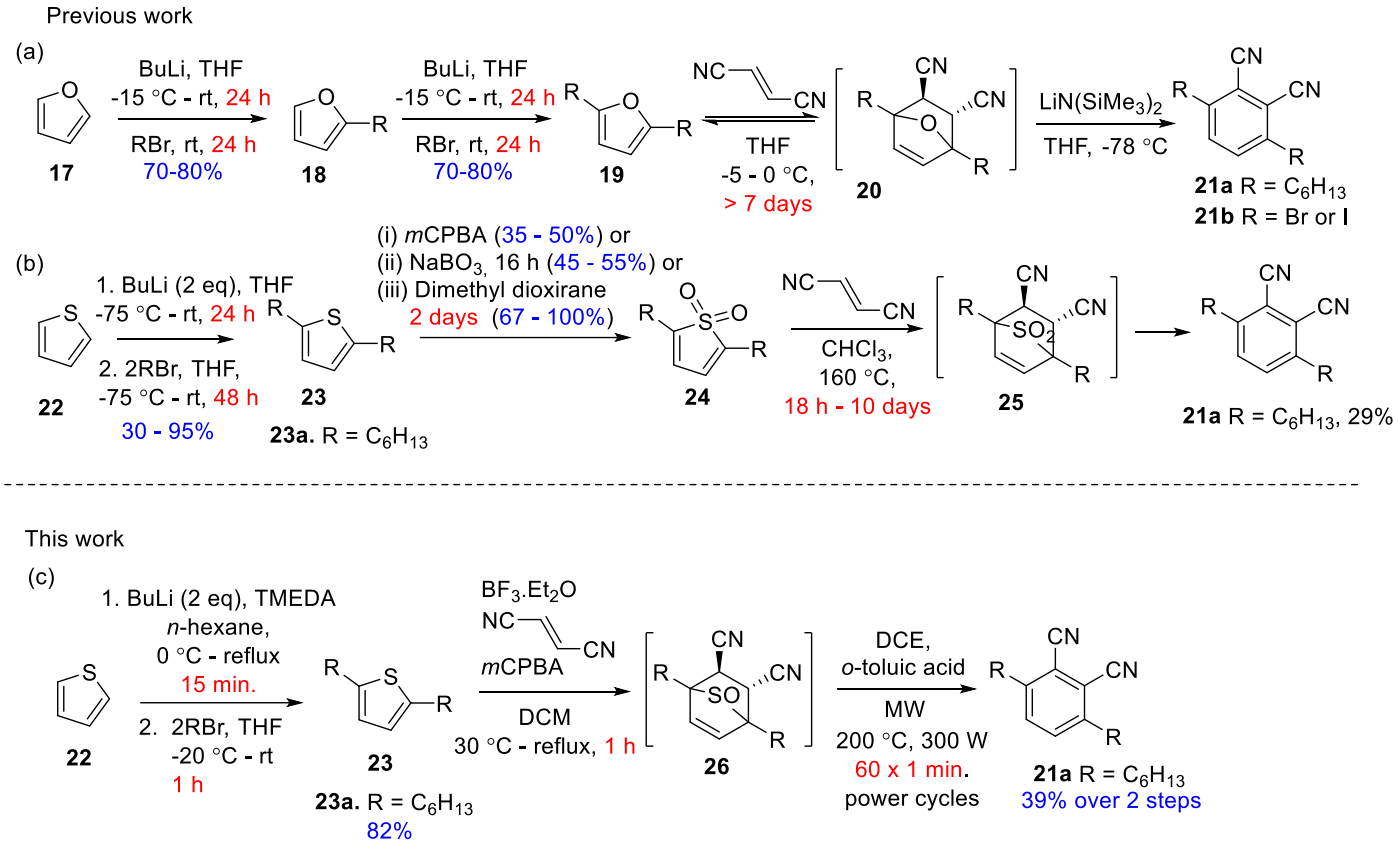
Scheme 2. Synthetic pathways to 4,5-dialkylphthalonitriles (**16**). *dppp = 1,3-bis(diphenylphosphino)propane, dba = dibenzylideneacetone ; dppf = 1,1'-bis(diphenylphosphino)ferrocene ; PMHS = polymethylhydrosiloxane*

3,6-Dialkylphthalonitriles (21a). The starting material for the non-peripheral alkyl substituted Pc's, 3,6-dihalophthalonitrile (2**1b**), is not commercially available and though the preparation of the 3,6-dibromo-[23] and 3,6-diiodophthalonitrile[24,25] have been documented, no reports for the application thereof in the preparation of 3,6-dialkylphthalonitriles (**21**) could be found. We therefore decided to apply the reliable Diels Alder strategy to the synthesis of 3,6-dialkylphthalonitriles (**21**).

The most common method to prepare 3,6-dialkylphthalonitriles (like **21a**) is based on the Diels-Alder reaction of fumaronitrile with a suitably substituted furan (**19**)[26-29] or thiophene 1,1-dioxide (**24**).[Error! Bookmark not defined.,Error! Bookmark not defined.,30-33] As the Diels-Alder reaction of the dialkylated furan (**19**) with fumaronitrile is reversible (Scheme 3a), the thiophene route is preferred (Scheme 3b). Each of the four steps in this route, i.e. lithiation, alkylation, sulfone oxidation and the Diels-Alder reaction with fumaronitrile, is extremely slow and typically requires days to run to completion.[34,35] Herein we report on a modified process that allows access to 3,6-dihexylphthalonitrile (**21a**) from (**22**) within 3 hours and in 32% overall yield (Scheme 3c). Lithiation of thiophene **22** with *n*-BuLi in hexane and tetramethylethylenediamine (TMEDA), rather than THF, afforded the lithium dianion within 15 minutes under reflux conditions. 1-Bromohexane was introduced at -20 °C following dilution with THF to give **21a** at ambient temperature in 82% yield within 1 hour.

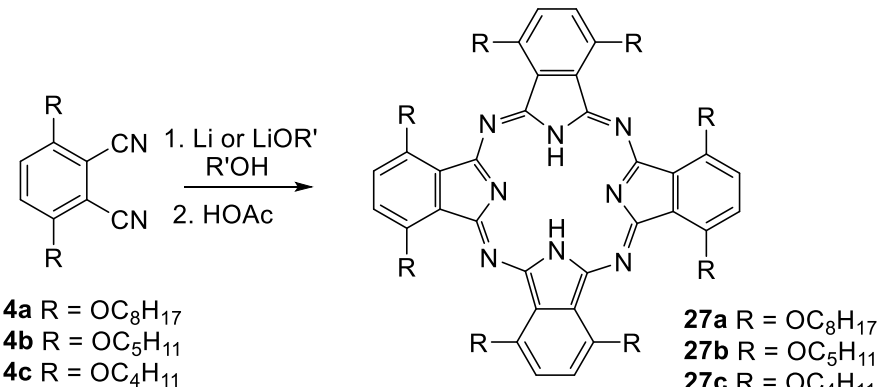
By disrupting the aromaticity of thiophene through oxidation of the sulphur atom, it may function as a diene in Diels-Alder reactions.[36] The Diels-Alder reaction of thiophene 1,1-dioxide (**24**) with fumaronitrile is very sluggish, though.[23,28,30,31] A theoretical study by Jursic[36] indicated the HOMO energy of thiophene 1-oxide to be higher than that of thiophene 1,1-dioxide, thus confirming it to be more electron-rich than the latter. In this regard, Thiemann and co-workers[37-39] reported a one-pot oxidation-cycloaddition procedure wherein $BF_3.OEt_2$ by coordinating to the *S*-monoxide oxygen and decreasing the nucleophilicity of the sulphur atom, prevents over-oxidation to the dioxide in the presence of *meta*-chloroperbenzoic acid (mCPBA).[Error! Bookmark not defined.,Error! Bookmark not defined.] The Lewis acid may, in addition, decrease the energy of the dienophile LUMO.[Error! Bookmark not defined.] By applying this concept in a novel oxidation - Diels-Alder reaction of substituted thiophene (**23**) with fumaronitrile, the crude 2,3-dicyano-1,4-dihexyl-7-thiabicyclo[2.2.1]hept-5-ene *S*-oxide (**26**) could be obtained within 1 hour (as opposed to days reported for the *S*-dioxide method). The intermediate substituted *S*-oxide (**26**) could furthermore be converted into the desired 1,4-dialkylphthalonitrile (**21**) within an hour via a microwave irradiation process (Scheme 3c).

Cyclotetramerization to H_2Pc. The Linstead method[40] for the tetramerization of phthalonitriles by lithium alkoxides, which dates back to 1934, is still commonly used.[4,Error! Bookmark not defined.,Error! Bookmark not defined.] Modifications of this method increased the yield of H_2Pc octasubstituted in the non-peripheral position with octyloxy substituents from 8 to 47% yield, for example. Following the procedure reported by McKeown and co-workers,[26.27] 3,6-dioctyloxyphthalonitrile (**4a**) was exposed to lithium metal in pentan-1-ol at reflux for 2 hours to afford the desired H_2Pc (**27a**), after treatment with acetic acid to exchange the lithium ions with hydrogens, in low yield (ca. 8%) (Table 3, entry 1). As only two equivalents of base are required according to the commonly accepted mechanism for tetramerization,[41-43] the Li equivalents were reduced to 2.5. This resulted in the desired octaoctyloxy Pc (**27a**), which were accompanied by Pcs where some of the octyloxy groups were substituted by pentoxy groups, to be obtained in 34% yield after 3 hours (Table 3, entry 2). The next logical choice was to form the lithium alkoxide prior to the introduction of the phthalonitrile, which afforded the desired H_2Pc (**27a**) in 47% yield (Table 3, entry 3). The optimized method was extended to the preparation of non-peripherally octasubstituted H_2Pc with pentoxy (**27b**) and butoxy substituents (**27c**), as well hexyl substituents (**27d**), in 56, 64 and 34% yield, respectively.



Scheme 3. Synthetic pathways to 3,6-dialkylphthalonitriles (**21**)

Table 3. The preparation of non-peripheral octasubstituted H_2Pc



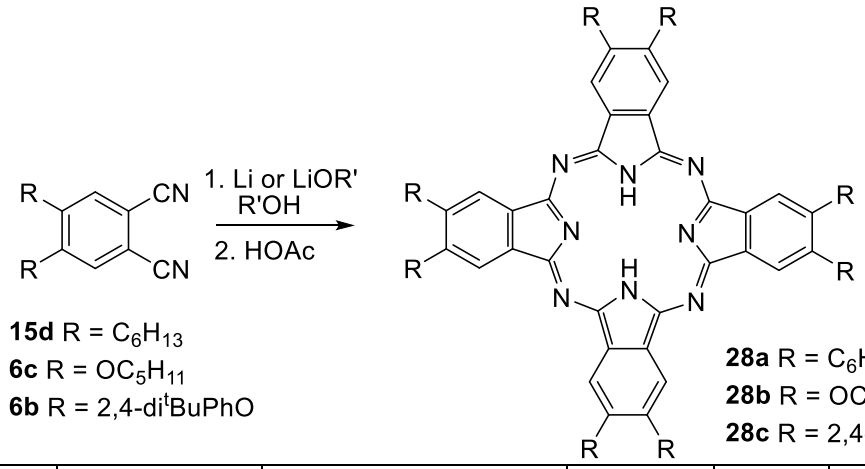
4a R = OC_8H_{17}
4b R = OC_5H_{11}
4c R = OC_4H_{11}
21a R = C_6H_{13}

27a R = OC_8H_{17}
27b R = OC_5H_{11}
27c R = OC_4H_{11}
27d R = C_6H_{13}

Entry	R	ROH	Li / LiOR	T (°C)	t (h)	Product	Yield (%)
1	OC_8H_{17}	pentan-1-ol	Li (25 eq)	138	2	**27a**	8
2	OC_8H_{17}	octan-1-ol	Li (2.5 eq)	140	3	**27a**	34
3	OC_8H_{17}	octan-1-ol	$LiOC_8H_{17}$ (2.5 eq)	140	3	**27a**	47
4	OC_5H_{11}	pentan-1-ol	$LiOC_5H_{11}$ (2.5 eq)	140	0.75	**27b**	56
5	OC_4H_{11}	butan-1-ol	$LiOC_4H_9$ (2.5 eq)	118	6	**27c**	64
6	C_6H_{13}	pentan-1-ol	$LiOC_5H_{11}$ (2.9 eq)	140	8	**27d**	34

Similarly, peripherally octa-substituted H_2Pc with hexyl (**28a**), pentoxy (**28b**) and 2,4-*t*-butylphenoxy substituents (**27c**) could be obtained in yields of 37, 57 and 38%, respectively (Table 4).

Table 4. The preparation of peripheral octasubstituted H_2Pc



15d R = C_6H_{13}
6c R = OC_5H_{11}
6b R = 2,4-di^{t}BuPhO

28a R = C_6H_{13}
28b R = OC_5H_{11}
28c R = 2,4-di^{t}BuPhO

Entry	R	ROH	Li / LiOR	T (°C)	t (h)	Product	Yield (%)
1	C_6H_{13}	pentan-1-ol	$LiOC_6H_{13}$ (2.5 eq)	138	4	**28a**	37
2	OC_5H_{11}	pentan-1-ol	$LiOC_5H_{11}$ (2.5 eq)	138	4	**28b**	57
3	2,4-di^{t}BuPhO	pentan-1-ol	$LiOC_5H_{11}$ (2.1 eq)	138	1	**28c**	38

When compared to reported accounts, all of these H_2Pcs can now be obtained in significantly higher yield, in less steps and/or in reduced reaction times (Table 5).

Table 5. Comparison of reported methodology for Pc synthesis with methodology and yields obtained in the current study

Entry	Compound	*Reported*			*Current study*		
		Starting material	Process steps	Overall Yield (%)	Starting material	Process steps	Overall Yield (%)
1	np-OC_8H_{17}- H_2Pc (**27a**)	(**3**)	2	19[8]	(**3**)	2	47
2	np-OC_5H_{11}- H_2Pc (**27b**)	(**3**)	2	28[44]	(**3**)	2	47
3	np-C_6H_{13}- H_2Pc (**27d**)	(**22**)	4	1.4[26]	(**22**)	3	11
4	p-C_6H_{13}- H_2Pc (**28a**)	(**12**)	4	7[20]	(**5**)	2	13
5	p-OC_5H_{11}- H_2Pc (**28b**)	(**7**)	4	14[45]	(**7**)	4	38
6	p-2,4-di^{t}BuPhO – H_2Pc (**28c**)	-[a]	-[a]	-[a]	(**5**)	2	30

[a]Metal-free Pc not reported. Np = non-peripheral, p = peripheral

Conclusions

Minor modifications to conventional synthetic routes allow simplified and quicker access to symmetrical peripheral and non-peripheral octaalkyl- and octaalkoxysubstituted H_2Pcs in better yields. Compared to literature reports, overall yields of octa-substituted H_2Pcs with alkoxy substituents (peripheral or non-peripheral), i.e. 1,4,8,11.15,18,22,25-octaoctyloxyphthalocyanine (**27a**), 1,4,8,11.15,18,22,25-octapentoxyphthalocyanine (**27b**) and 2,3,9,10,16,17,23,24-octapentoxyphthalocyanine (**28b**) could be improved from 19%,[8] 28%[44] and 14%[45] to 47%, 47% and 38%, respectively. Analogous octa-substituted H_2Pcs with alkyl substituents, 1,4,8,11.15,18,22,25-octahexylphthalocyanine (**27d**) and 2,3,9,10,16,17,23,24-octahexylphthalocyanine (**28a**), could be prepared in less steps in overall yields of 11% and 13%, respectively, as opposed to reported yields of 1.4%[26] and 7%.[20] The novel 2,3,9,10,16,17,23,24-octakis(2,4-di-*tert*-butylphenoxy)phthalocyanine (**28c**) could in addition be prepared in two steps in 30% overall yield. The modified processes may be of industrial significance with regards to applications in dyes, photodynamic cancer therapy, photochemical and photovoltaic cells, laser printing, optical communication and catalysis, for example.

Experimental Section

General. NMR-spectroscopy was performed on a Bruker AM 600 FT-spectrometer at 293 K (unless specified to the contrary) with either $CDCl_3$ (deuterochloroform), $(CD_3)_2CO$ (deuterated acetone) or C_6D_6 (deuterobenzene) as solvent. Chemical shifts are reported in parts per million (ppm) with the solvent peak at 7.26 ppm for $CDCl_3$, 2.05 ppm for $(CD_3)_2CO$ or 7.16 ppm for C_6D_6 in ^1H, and 77.16 ppm for $CDCl_3$, 206.26 ppm for $(CD_3)_2CO$ and 128.06 ppm for C_6D_6 in ^{13}C NMR experiments. Coupling constants are given in Hz. Mass spectrometry was performed by means of electron impact (EI) ionization on a Shimadzu GC-MS QP-2010 by means of a direct sample inlet unit (DI-2010). Alternatively, MS was performed with a Matrix Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) Bruker Microflex LRF20 in either the

positive or negative mode with the minimum laser (337 nm) power required to observe signals. Spectra obtained were compared to simulated data generated by Bruker Daltonics Molecular Formula Generator 1.0 software. High resolution MS (EI-MS, 70 eV) was performed by PMBMS, University of KwaZulu-Natal or North-West University, South Africa. Infrared spectra (IR) were acquired on a Digilab FTS 2000 infrared spectrometer. Ultraviolet-visible spectroscopy (UV-Vis) analysis were conducted on either a Cary 50 or a Cary 500 UV-Vis spectrophotometer over a wavelength range of 300 – 800 nm. The absorption values of several standard solutions (0.12 – 250.00 µM) in toluene were used to determine the absorption coefficients (ε) by means of the Beer-Lambert law. Elemental analysis was conducted by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada. Melting points were determined with a Barloworld Scientific Stuart Melting Point (SMP3) apparatus and are uncorrected. Microwave reactions were carried out in a CEM Discover® SP microwave reactor utilising the dynamic irradiation program (fixed temperature, variable power) with continuous cooling and the power set to a maximum of 200 W.

Standardization of BuLi and Grignard reagents

Triphenylmethane or 2,2'-bypiridine (8-10 mg) was dissolved in dry 1,4-dioxane (4 mL). A double-burette titration was performed with BuLi or Grignard and dry 1-pentanol (0.05 mL). The endpoint of the titration was presented with a colour change from colourless to red or orange. All titrations were performed in triplicate.

3,6-Dioctyloxyphthalonitrile (4a). Based on previously reported etherification procedures,[8,46] a solution of 3,6-dihydroxyphthalonitrile (**3**) (0.51 g, 2.5 mmol), K_2CO_3 (1.38 g, 9.8 mmol, 4.0 eq.), KI (0.17 g, 0.5 mmol, 0.2 eq.) and octyl bromide (1.2 mL, 6.9 mmol, 3.0 eq.) in dry DMF (25 mL) was kept at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature prior to acidification with 3 M HCl (1 L/100 mL DMF). The resultant mixture was stirred for 15 minutes, whereafter the cream precipitate was collected and washed with water. Recrystallization (EtOAc : EtOH 1:1) afforded 3,6-dioctyloxyphthalonitrile **(4a)** as white needles (0.95 g, 99%): mp 146-148 °C (lit.[8] 147 °C); R*f* 0.88 (Hexanes : Acetone, 6:4); ^{1}H NMR (600 MHz, $CDCl_3$)[46] δ 7.15 (2H, s, H-4,5), 4.04 (4H, t, *J* = 6.5 Hz, H-1'), 1.84 – 1.79 (4H, m, H-2'), 1.50 – 1.44 (4H, m, H-3'), 1.36 – 1.24 (16H, m, H-4',5',6',7'), 0.88 (6H, t, *J* = 7.0 Hz, H-8'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3 (C-3,6), 118.7 (C-4,5), 113.2 (*C*N), 105.4 (C-1,2), 70.4 (C-1'), 31.9, 29.3, 29.3, 29.0, 25.9 (C-3'), 22.8, 14.2 (C-8'); IR ν (neat, cm^{-1})[8] 2227 (CN); EIMS (70 eV) *m/z* 384 (M^+, 13%).

3,6-Dipentoxyphthalonitrile (4b). A solution of 3,6-dihydroxyphthalonitrile (**3**) (1.53 g, 7.4 mmol), K_2CO_3 (4.09 g, 29.6 mmol, 4.0 eq.), KI (0.31 g, 1.9 mmol, 0.3 eq.) and pentyl bromide (3.0 mL, 24.2 mmol, 3.3 eq.) in dry DMF (30 mL) was kept at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature prior to acidification with 3 M HCl (1 L/100 mL DMF). The resultant mixture was stirred for 15 minutes, whereafter the cream precipitate was collected and washed with water. Recrystallization (EtOAc : EtOH 1:1) afforded 3,6-dipentoxyphthalonitrile **(4b)** as white needles (2.39 g, 83%): mp 171-173 °C (lit.[8] 172 °C); R*f* 0.28 (Hexanes : Acetone, 8:2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (2H, s, H-4,5), 4.04 (4H, t, *J* = 6.5 Hz, H-1'), 1.85 – 1.79 (4H, m, H-2'), 1.48 – 1.42 (4H, m, H-3'), 1.40 – 1.33 (4H, m, H-4'), 0.92 (6H, t, *J* = 7.3 Hz, H-5'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3 (C-3,6), 118.7 (C-4,5), 113.2 (*C*N), 105.1 (C-1,2), 70.3 (C-1'), 28.7 (C-2'), 28.0 (C-3'), 22.4 (C-4'), 14.0 (C-5'); IR ν (neat, cm^{-1}) 2226 (CN); EIMS (70 eV) *m/z* 300 (M^+, 20%).

3,6-Dibutoxyphthalonitrile (4c). A solution of 3,6-dihydroxyphthalonitrile (**3**) (1.02 g, 6.4 mmol), K_2CO_3 (2.67 g, 19.4 mmol, 3.0 eq.), KI (0.38 g, 2.3 mmol, 0.4 eq.) and butyl bromide (1.65 mL, 15.3 mmol, 2.4 eq.) in dry DMF (20 mL) was kept at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature prior to acidification with 3 M HCl (1 L/100 mL DMF). The resultant mixture was stirred for 15 minutes, whereafter the cream precipitate was collected and washed with water. Recrystallization (EtOAc

: EtOH 1:1) afforded 3,6-dibutoxyphthalonitrile **(4c)** as white needles (1.45 g, 84%): mp 191-193 °C (lit.[8] 193 °C); R*f* 0.38 (Hexanes : EtOAc, 7:3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (2H, s, H-4,5), 4.05 (4H, t, *J* = 6.4 Hz, H-1'), 1.83-1.75 (4H, m, H-2'), 1.55-1.46 (4H, m, H-3'), 0.96 (6H, t, *J* = 7.4 Hz, H-4'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3 (C-3,6), 118.8 (C-4,5), 113.2 (*C*N), 105.0 (C-1,2), 70.0 (C-1'), 31.0 (C-2'), 19.1 (C-3'), 13.8 (C-4'); IR ν (neat, cm^{-1}) 2226 (CN); EIMS (70 eV) *m/z* 272 (M^+, 100%).

4,5-Bis(2,4-di-*tert*-butylphenoxy)phthalonitrile (6b). A solution of 4,5-dichlorophthalonitrile (**5**) (1.00 g, 5.08 mmol), K_2CO_3 (4.91 g, 35.5 mmol, 7 eq.) and 2,4-di-*tert*-butylphenol (2.20 g, 10.7 mmol, 2.1 eq.) in dry DMF (75 mL) was kept at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature prior to acidification with 3 M HCl (1 L/100 mL DMF). The resultant mixture was stirred for 15 minutes, whereafter the cream precipitate was collected and washed with water. Recrystallization (EtOAc : EtOH 1:1) afforded 4,5-bis(2,4-di-*tert*-butylphenoxy)phthalonitrile **(6b)** as white needles (2.11 g, 78%): mp 191-193 °C (lit.[8] 193 °C); R*f* 0.38 (Hexanes : EtOAc, 7:3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (2H, s, H-4,5), 4.05 (4H, t, *J* = 6.4 Hz, H-1'), 1.83-1.75 (4H, m, H-2'), 1.55-1.46 (4H, m, H-3'), 0.96 (6H, t, *J* = 7.4 Hz, H-4'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3 (C-3,6), 118.8 (C-4,5), 113.2 (*C*N), 105.0 (C-1,2), 70.0 (C-1'), 31.0 (C-2'), 19.1 (C-3'), 13.8 (C-4'); IR ν (neat, cm^{-1}) 2226 (CN); EIMS (70 eV) *m/z* 272 (M^+, 100%).

Preparation of 4,5-dialkoxyphthalonitriles

1,2-Dipentoxybenzene (9). A solution of catechol (**7**) (5.03 g, 45.8 mmol), K_2CO_3 (31.75 g, 230.1 mmol, 5.0 eq.), KI (0.75 g, 4.5 mmol, 0.1 eq.) and pentyl bromide (12.0 mL, 96.8 mmol, 2.1 eq.) in dry DMF (100 mL) was kept at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature prior to acidification with 3 M HCl (1 L/100 mL DMF). The resultant mixture was stirred for 15 minutes and the product extracted into EtOAc (3 x 15 mL). The combined organic phases were washed with water (20 mL), saturated aq. $NaHCO_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated in vacuo to afford 1, 2-dipentoxybenzene (**9**) as a light yellow oil (10.58 g, 93%): R*f* 0.76 (Hexanes : Acetone, 8:2); ^{1}H NMR (600 MHz, $CDCl_3$)[47] δ 6.92-6.90 (4H, m, H- Ar); 4.02 (4H, t, *J* = 6.7 Hz, H-1'); 1.88-1.82 (4H, m, H-2'), 1.52-1.46 (4H, m, H-3'); 1.45-1.38 (4H, m, H-4'); 0.96 (6H, t, *J* = 7.3 Hz, H-5'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.3 (C-1,2), 121.1, 114.1, 69.3 (C-1'), 29.1 (C-2'), 28.3 (C-3'), 22.6 (C-4'), 14.1 (C-5') ; EIMS (70 eV) *m/z* 250 (M^+, 19%).

4,5-Dibromocatechol (8). A solution of Br_2 (5.0 mL; 98 mmol, 2.1 eq) in DCM (15 mL) was added dropwise to a cooled (0 °C) solution of catechol (**7**) (5.01 g, 45.6 mmol) in DCM (100 mL). The solution was allowed to warm to r.t. and stirring continued overnight. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (until no bubbling could be observed), saturated aqueous $Na_2S_2O_5$ (until no bubbling could be observed) and H_2O (100 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure at *ca*. 25 °C. Flash column chromatography (Hexanes : DCM 1:1) afforded 1,2-dibromocatehol (**8**) as a grey powder (11.99 g, 98%): mp 94-96 °C (lit.[48] 97-98 °C); R*f* 0.05 (H:DCM, 1:1); ^{1}H NMR (600 MHz, C_3D_6O)[48] δ 7.14 (2H, s, H-3,6); ^{13}C NMR (151 MHz, C_3D_6O) δ 146.2, 119.8 (C-3,6), 112.6; EIMS (70 eV) *m/z* 268 (M^+, 100%).

1,2-Dibromo-4,5-dipentoxybenzene (10)

(i) Etherification

A solution of 4,5-dibromocatechol (**8**) (9.98 g, 37.2 mmol), K_2CO_3 (25.78 g, 186.8 mmol, 5.0 eq.), KI (0.76 g, 4.6 mmol, 0.1 eq.) and pentyl bromide (9.8 mL, 79.0 mmol, 2.1 eq.) in dry DMF (100 mL) was kept at 80 °C overnight. The reaction mixture was allowed to cool to ambient temperature prior to acidification with 3 M HCl (1 L/100 mL DMF). The resultant mixture was stirred for 15 minutes and the product extracted into EtOAc (3 x 15 mL). The combined organic phases were washed with water (20 mL), saturated aq. NaHCO3 (20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Crystallization (EtOH) afforded 1,2-dibromo-4,5-dipentoxybenzene (**10**) as colourless needles (12.37g, 82%): mp 28-30 °C (lit.[49] 45-47 °C);

R*f* 0.83 (Hexanes : DCM, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (2H, s, H-3,6), 3.95 (4H, t, *J* = 6.6 Hz, H-1'), 1.84-1.79 (4H, m, H-2'), 1.48-1.36 (8H, m, H-3',4'), 0.94 (6H, t, *J* = 7.2 Hz, H-5'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0 (C-4,5), 117.9 (C-3,6), 114.7 (C-1,2), 69.6 (C-1'), 28.8 (C-2'), 28.1 (C-3'), 22.4 (C-4'), 14.1 (C-5'); EIMS (70 eV) *m/z* 408 (M^+, 42%).

(ii) Bromination

A solution of Br_2 (4.3 mL; 83.9 mmol, 2.0 eq) in DCM (15 mL) was added dropwise to a cooled (0 °C) solution of 1,2-dipentoxybenzene (**9**) (10.37g, 41.4 mmol) in DCM (100 mL). The solution was allowed to warm to r.t. and stirring continued overnight. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (until no bubbling could be observed), saturated aqueous $Na_2S_2O_5$ (until no bubbling could be observed) and H_2O (100 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure at *ca*. 25 °C. Flash column chromatography (Hexanes : DCM 1:1) afforded 1,2-dibromo-4,5-dipentoxybenzene (**10**) as colourless needles (14.33 g, 89%): See (i).

1,2-Diiodo-4,5-dipentoxybenzene (11). A solution of 4,5-dipentoxybenzene (**9**) (5.00 g, 20.0 mmol), $NaIO_4$ (1.72 g, 8.0 mmol, 0.4 eq.) and I_2 (4.58 g, 18.0 mmol, 0.9 eq.) in $HOAc:H_2O:H_2SO_4$ (100:20:3; 12 mL) was heated at 70 °C until no I_2 sublimation could be observed. The reaction mixture was cooled to r.t. and extracted with EtOAc (3 x 50 mL). The organic phase was washed with aqueous $NaHCO_3$ (until no bubbling could be observed), aqueous $Na_2S_2O_4$ (until colourless) and the organic phase washed with H_2O (50 mL) and brine (50mL). After drying the EtOAc layer with Na_2SO_4, all solvent was removed *in vacuo* (*ca*. 40 °C). Flash column chromatography (Hexanes : DCM 1:1) afforded 1,2-diiodo-4,5-dipentoxybenzene (**11**) as a colourless oil (9.24 g, 92%): R*f* 0.77 (Hexanes : DCM, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (2H, s, H-3,6), 3.92 (4H, t, *J* = 6.6 Hz, H-1'), 1.82 – 1.76 (4H, m, H-2'), 1.45 – 1.34 (8H, m, H-3',4'), 0.92 (6H, t, *J* = 7.2 Hz, H-5'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8 (C-4,5), 123.8 (C-3,6), 96.1 (C-1,2), 69.5 (C-1'), 28.8 (C-2'), 28.2 (C-3'), 22.5 (C-4'), 14.1 (C-5'); EIMS (70 eV) *m/z* 502 (M^+, 52%); HRMS (*m/z*) Cald for $C_{16}H_{24}O_2NaI_2$ $(M + Na)^+$ 524.9764, found 524.9767.

4,5-Dipentoxyphthalonitrile (6c)

(i) Rosenmund-von Braun cyanation

A solution of 1,2-dibromo-4,5-dipentoxybenzene (**10**) (0.45 g, 1.1 mmol) and CuCN (0.43 g, 4.8 mmol, 4.4 eq.) in dry DMF (5 mL) was kept at 140 °C overnight. The reaction mixture was cooled to r.t. and diluted with 25 % NH_4OH (100 mL). The blue aqueous solution was extracted with EtOAc (3 x 50 mL) and the organic fractions combined. The latter was acidified with 3M HCl (100 mL), after which neutralization with saturated aqueous $NaHCO_3$ was conducted (litmus paper). The organic solvent was dried over Na_2SO_4, the solvent removed *in vacuo* at *ca*. 40 °C. Flash column chromatography (Hexanes : DCM 1:1) afforded 4,5-dipentoxyphthalonitrile (**6c**) as white flakes (0.10 g, 29%): mp 122-124 °C (lit.[49] 84-86 °C); R*f* 0.33 (Hexanes : DCM, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (2H, s, H-3,6), 4.04 (4H, t, *J* = 6.5 Hz, H-1'), 1.88 – 1.81 (4H, m, H-2'), 1.47 – 1.35 (8H, m, H-3',4'), 0.92 (6H, t, *J* = 7.2 Hz, H-5'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5 (C-4,5), 116.1, 115.8 (C-3,6), 108.3, 69.8 (C-1'), 28.4 (C-2'), 28.0 (C-3'), 22.4 (C-4'), 14.0 (C-5'); IR ν (neat, cm^{-1})[6] 2230 (CN); EIMS (70 eV) *m/z* 300 (M^+, 20%).

Repeating the procedure with 1,2-diiodo-4,5-dipentoxybenzene (**11**) (0.50 g, 1.0 mmol) and CuCN (0.36 g, 4.0 mmol, 3.7 eq.) afforded the title compound as white flakes (0.16 g, 52%): See above.

(ii) Negishi cyanation

A solution of 1,2-dibromo-4,5-dipentoxybenzene (**10**) (0.42g, 1.0 mmol) and PMHS (24 µL) in DMA (2 mL) was heated to 120 °C under Ar flow. $Pd_2(dba)_3$ (0.02g, 21.8 mmol, 2.1 mol%) and dppf (0.02 g, 32.3 µmol, 3.2 mol%) was added and the mixture stirred for 10 min. $Zn(CN)_2$ (0.14 g, 1.2 mmol, 1.2 eq.) was added in portions with 15-20 min intervals over 2 hours. After stirring for an additional 2 hours the reaction mixture was acidified with 3 M HCl (10 mL/mmol) and extracted with EtOAc (3 x 20 mL). The organic layers were combined, washed with H_2O (10 mL), neutralized with saturated aqueous $NaHCO_3$ (litmus paper), washed with brine and dried over Na_2SO_4. All solvent was removed *in vacuo* (*ca*. 40 °C), whereafter recrystallization from a minimum amount of DCM and hexane (50 mL) afforded 4,5-dipentoxyphthalonitrile (**6c**) as white flakes (0.25 g, 80%): R*f* 0.53 (Hexanes : DCM, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (1H, s, H-3/6), 7.03 (1H, s, H-3/6), 4.00 (2H, t, *J* = 6.6 Hz, H-1'/1''), 3.95 (2H, t, *J* = 6.6 Hz, H-1'/1''), 1.87 – 1.78 (4H, m, H-2',2''), 1.48 – 1.35 (8H, m, H-3',3'',4',4''), 0.92 (3H, t, *J* = 7.2 Hz, H-5'/5''), 0.92 (3H, t, *J* = 7.2 Hz, H-5'/5''); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 148.4, 118.0, 117.4, 117.1 (C-3/6), 116.7 (C-3/6), 106.5, 69.7 (C-1'/1''), 69.6 (C-1'/1''), 28.7, 28.7, 28.2, 28.1, 22.5, 22.4, 14.1 (C-5'/5''), 14.1 (C-5'/5''); IR ν (neat, cm^{-1}) 2230 (CN); EIMS (70 eV) *m/z* 353 (M^+, 22%); HRMS (*m/z*) Calcd for $C_{17}H_{24}BrNO_2Na$ $(M + Na)^+$ 376.0888, found 376.0888.

Repeating the procedure with 1,2-diiodo-4,5-dipentoxybenzene (**11**) (0.50 g, 1.0 mmol), PMHS (24 µL), $Pd_2(dba)_3$ (0.02g, 21.8 mmol, 2.1 mol%), dppf (0.02 g, 27.5 µmol, 2.7 mol%) and $Zn(CN)_2$ (0.12 g, 1.4 mmol, 1.4 eq.) afforded 4,5-dipentoxyphthalonitrile (**6c**) as white flakes (0.17 g, 56%): See above.

Preparation of 4,5-dihexylphthalonitrile (15d)

1,2-Dihexylbenzene (13a). *n*-Hexyl bromide (13 mL, 95.5 mmol, 2.7 eq.) was dissolved in dry Et_2O (10 mL). This solution (1 mL) was added to magnesium filings (2.21 g, 92.2 mmol, 2.6 eq.) in dry Et_2O (35 mL). After initiation of the reaction, the mixture was cooled in an ice bath and the remaining n-hexyl bromide solution added dropwise at such a rate as to maintain a gentle reflux. After addition was complete, the reaction mixture was refluxed for 1h. The freshly prepared Grignard solution was cooled and added dropwise to an ice cold solution of 1,2-dichlorobenzene (**12**) (4 mL, 35.4 mmol) and $Ni(dppp)Cl_2$ (0.07 g, 0.1 mmol, 0.3 mol%) in dry Et_2O (30 mL) over 10 min. The reaction mixture was allowed to warm to room temperature over 1 hour after which it was heated to reflux for 6 hours. The reaction mixture was cooled in an ice bath prior to dropwise addition of H_2O (10 mL) and 3M HCl (10 mL). The organic phase was washed with H_2O (20 mL), saturated aq. $NaHCO_3$ (20 mL) and brine (20 mL) followed by drying over Na_2SO_4. The solvent was removed in vacuo and the crude product distilled to afford 1,2-dihexylbenzene (**13a**) as a colourless oil (4.92 g, 57%): R*f* 0.69 (Hexanes); ^{1}H NMR (600 MHz, $CDCl_3$)[13] δ 7.19 – 7.13 (1H, m, Ar-H), 2.65 – 2.61 (4H, m, H-1'), 1.64 – 1.58 (4H, m, H-2'), 1.45 – 1.39 (4H, m, H-3'), 1.39 – 1.33 (8H, m, H-4',5'), 0.96 – 0.91 (6H, m, H-6'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.7 (C-1,2), 129.3 (C-4,5), 125.8 (C-3,6), 32.9 (C-1'), 31.9 (C-2'), 31.5 (C-3'), 29.7 (C-4'), 22.8 (C-5'), 14.3 (C-6'); EIMS (70 eV) *m/z* 246 (M^+, 18%).

1,2-Diiodo-4,5-dihexylbenzene (15a). A solution of 1,2-dihexylbenzene (**13a**) (1.99 g, 8.1 mmol), $NaIO_4$ (0.80 mg, 3.7 mmol, 0.5 eq.) and I_2 (2.31 g, 9.1 mmol, 1.1 eq.) in $HOAc:H_2O:H_2SO_4$ (150:9:1; 32 mL) was heated at reflux until no I_2 sublimation could be observed. The reaction mixture was cooled to r.t. and extracted with EtOAc (3 x 50 mL). The organic phase was washed with aqueous $NaHCO_3$ (until no bubbling could be observed), aqueous $Na_2S_2O_4$ (until colourless) and the organic phase washed with H_2O (50 mL) and brine (50 mL). After drying the EtOAc layer with Na_2SO_4, all solvent was removed *in vacuo* (*ca*. 40 °C). Flash column chromatography (Hexanes : DCM 1:1) afforded 1,2-diiodo-4,5-dihexylbenzene (**15a**) as a white amorphous solid (2.59 g, 64%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (1H, s, H-3,6), 2.48 – 2.45 (2H, m, H-1'), 1.54 – 1.48 (2H, m, H-2'), 1.38 – 1.28 (6H, m, H-3',4',5'), 0.89 (3H, t, J = 6.9 Hz, H-6'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9 (C-4,5), 139.9 (C-3,6), 104.1 (C-1,2), 32.1, 31.8, 31.1, 29.4, 22.7, 14.2 (C-6'); EIMS (70 eV) *m/z* 498 (M^+, 100%).

4,5-Dihexylphthalonitrile (16d)

(i) Rosenmund-von Braun cyanation

A solution of 1,2-diiodo-4,5-dihexylbenzene (**15a**) (0.40 g, 0.8 mmol) and CuCN (0.22 g, 2.4 mmol, 3.0 eq.) in dry DMF (4 mL) was kept at 140 °C overnight. The reaction mixture was cooled to r.t. and diluted with 25 % NH_4OH (100 mL). The blue aqueous solution was extracted with EtOAc (3 x 50 mL) and the organic fractions combined. The latter was acidified with 3M HCl (100 mL), after which neutralization with saturated aqueous $NaHCO_3$ was conducted (litmus paper). The organic solvent was dried over Na_2SO_4, the solvent removed *in vacuo* at *ca*. 40 °C. Flash column chromatography (Hexanes : DCM 1:1) afforded 4,5-dihexylphthalonitrile (**16d**) as a light peach coloured oil (0.21 g, 87%): R_f 0.57 (Toluene); ^{1}H NMR (600 MHz, $CDCl_3$)[20] δ 7.55 (2H, s, H-3,6), 2.67 (4H, t, *J* = 8.04 Hz, H-1'), 1.59 – 1.53 (4H, m, H-2'), 1.41 – 1.34 (4H, m, H-3'), 1.33 – 1.29 (8H, m, H-4',5'), 0.89 (6H, t, *J* = 7.1 Hz, H-6'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5 (C-4,5), 134.0 (C-3,6), 115.9 (-C), 112.8 (C-1,2), 32.6 (C-1'), 31.6 (C-4'/5'), 30.4 (C-2'), 29.2 (C-3'), 22.5 (C-4'/5'), 14.1 (C-6'); IR ν (neat, cm^{-1}) 2233 (CN); EIMS (70 eV, *m/z*) 296 (M^+, 60%).

(ii) Negishi cyanation

A solution of 1,2-diiodo-4,5-dihexylbenzene (**15a**) (1.00 g, 2.0 mmol) and PMHS (48 µL) in DMA (4 mL) was heated to 120 °C under Ar flow. $Pd_2(dba)_3$ (0.05 g, 0.05 mmol, 2.7 mol%) and dppf (0.04 g, 0.07 mmol, 3.6 mol%) was added and the mixture stirred for 10 min. $Zn(CN)_2$ (0.26 g, 2.2 mmol, 1.1 eq.) was added in portions with 15-20 min intervals over 2 hours. After stirring for an additional 2 hours the reaction mixture was acidified with 3 M HCl (10 mL/mmol) and extracted with EtOAc (3 x 20 mL). The organic layers were combined, washed with H_2O (10 mL), neutralized with saturated aqueous $NaHCO_3$ (litmus paper), washed with brine and dried over Na_2SO_4. All solvent was removed *in vacuo* (*ca*. 40 °C), whereafter flash column chromatography (Hexanes : DCM 1:1) afforded 4,5-dihexylphthalonitrile (**16d**) as a light peach coloured oil (0.25 g, 80%): See above.

(iii) S_NAr alkylation

Ethylmagnesium bromide (3M in Et_2O, 1.7 mL, 4 eq.) was added to a cooled (-10 °C) solution of $Fe(acac)_3$ (463 mg, 1.3 mmol, 1.0 eq.) and NMP (1.6 mL) in dry THF (16 mL) and stirring continued for 10 minutes prior to addition of the 4,5-dichlorophthalonitrile (**5**) (253 mg, 1.3 mmol). After 10 minutes, hexylmagnesium bromide (1.2 M in Et_2O, 2.1 mL, 2.5 mmol, 2.0 eq.) was added portionwise (5-10 minutes intervals) after which the temperature was maintained for 30 minutes. The reaction mixture was allowed to warm to r.t. over 4 hours after which 3 M HCl (20 mL/mmol) was added and extraction performed with EtOAc (3 x 20 mL/mmol). The organic fractions were combined, washed with H_2O (10 mL/mmol), saturated aqueous $NaHCO_3$ (10 mL/mmol) and brine (10 mL/mmol). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure (*ca*. 40 °C). Flash column chromatography (Toluene) afforded 4,5-dihexylphthalonitrile (**16d**) as light peach coloured oil (0.13 g, 36%): See above.

3,6-Dihexylphthalonitrile (21a)

2,5-Dihexylthiophene (23a). A solution of *n*-BuLi (2.1 M, 80 mL, 167.9 mmol, 2.2 eq.) in hexane was added to an ice cold solution of thiophene (**22**) (6 mL, 75.0 mmol) and TMEDA (14 mL, 91.3 mmol, 1.2 eq.) in dry hexane (60 mL). The cloudy reaction mixture was allowed to warm to room temperature and then refluxed for 30 min. The reaction mixture was cooled to room temperature, diluted with dry THF (180 mL) and cooled to -20 °C. Hexyl bromide (32 mL, 228.0 mmol, 3.0 eq.) was added dropwise over 5 min. and the reaction mixture allowed to reach room temperature. After stirring for 1 hour, the reaction mixture was transferred to ice water (500 mL) and extracted with Et_2O (3 x 200 mL). The organic phase was washed with brine (100 mL), dried over Na_2SO_4 and evaporated under reduced pressure at ca. 60 °C. Purification by

distillation (168 – 170 °C at 10 mmHg) afforded 2,5-dihexylthiophene (**23a**) as a colourless oil (15.59 g, 82%): R*f* 0.86 (Hexanes); ^{1}H NMR (600 MHz, $CDCl_3$)[50] δ 6.59 (2H, s, H-3,4), 2.78 (4H, t, *J* = 7.7 Hz, H-1'), 1.71 – 1.65 (4H, m, *J* = 15.3, 7.5 Hz, H-2'), 1.43 – 1.31 (12H, m, H-3',4',5'), 0.93 (6H, t, *J* = 7.0 Hz, H-6'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4 (C-3,4), 123.4 (C-2,5), 31.9 (C-2'), 31.8 (C-4'/5'), 30.3 (C-1'), 29.0 (C-3'), (C-4'/5'), 14.2 (C-6'); EIMS (70 eV) *m/z* 252 (M^+, 22.7 17%).

2,5-Dihexylthiophene 1,1-dioxide (24a). Solid *m*-CPBA (freshly recrystallized from DCM; 1.41 g, 8.2 mmol, 4.1 eq.) was added stepwise over 1 h to a vigorously stirred mixture of 2,5-dihexylthiophene (**23a**) (0.50 g, 2.0 mmol) and $NaHCO_3$ (0.67 g, 7.9 mmol, 4.0 eq.) in DCM (30 mL) at 0 °C. After completion of the reaction, the precipitate was filtered off and washed with DCM (2 x 5 mL). The filtrate was concentrated in vacuo, whereafter recrystallization (pentane) afforded 2,5-dihexylthiophene 1,1-dioxide (**24a**) as white needles (0.30 g, 54%): mp 45-47 °C (lit.[50] 41 °C); R*f* 0.63 (Hexanes : EtOAc, 8:2); ^{1}H NMR[50] (600 MHz, $CDCl_3$) δ 6.28 – 6.24 (2H, m, H-3,4), 2.46 (4H, t, *J* = 7.7 Hz, H-1'), 1.68 – 1.61 (4H, m, H-2'), 1.41 – 1.34 (4H, m, H-3'), 1.33 – 1.26 (8H, m, H-4',5'), 0.91 – 0.86 (6H, m, H-6'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1 (C-2,5), 121.8 (C-3,4), 31.5 (C-4'/5'), 28.9 (C-3'), 26.7 (C-2'), 24.4 (C-1'), 22.6 (C-4'/5'), 14.2 (C-6'); IR ν (neat, cm^{-1}) 1277 (SO_2), 1142 (SO_2); EIMS (70 eV) *m/z* 284 (M^+, 35%).

2,3-Dicyano-1,4-dihexyl-7-thiabicyclo[2.2.1]hept-5-ene *S*-oxide (26a). $BF_3.OEt_2$ (2 mL, 16.2 mmol, 6.0 eq.) was added to a cooled (-20 °C) solution of 2,5-dihexylthiophene (**23a**) (0.68 g, 2.7 mmol) and fumaronitrile (0.33 g, 4.2 mmol, 1.6 eq.) in dry DCM (10 mL) and the solution stirred for 20 min. A solution of *m*-CPBA (0.71 g, 4.1 mmol, 1.5 eq.) in dry DCM (15 mL) was added dropwise after which the solution was allowed to warm to room temperature and stirring continued for 48 h. The reaction mixture was quenched with H_2O (10 mL) and the organic phase stirred with saturated aqueous $NaHCO_3$ (10 mL) for 15 min. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography (Hexanes : EtOAc 8:2) afforded 2,3-dicyano-1,4-dihexyl-7-thiabicyclo[2.2.1]hept-5-ene *S*-oxide (**26a**) as a light yellow solid (0.59 g, 64%): R*f* 0.49 (Hexanes : EtOAc, 8:2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.34 (1H, d, *J* = 7.0 Hz, H-5/6), 6.27 (1H, d, *J* = 7.0 Hz, H-5/6), 3.92 (1H, d *J* = 5.2 Hz, H-2/3), 3.17 (1H, d, *J* = 5.2 Hz, H-2/3), 2.17 – 2.03 (3H, m, H-Alk.), 1.97 – 1.90 (1H, m, H-Alk.), 1.56 – 1.36 (8H, m, H-Alk.), 1.36 – 1.26 (8H, m, H-Alk.), 0.89 (3H, t, *J* = 7.0 Hz, 1 x -C*H*$_3$) , 0.89 (3H, t, *J* = 6.8 Hz, 1 x -C*H*$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2 (C-5/6), 132.1 (C-5/6), 117.3 (1 x -CN), 114.8 (1 x -CN), 76.6 (C-1/4), 75.5 (C-1/4), 39.5 (C-2/3), 38.6 (C-2/3), 31.5, 29.4, 29.4, 27.3, 27.0, 26.5, 26.3, 22.5, 14.1 (-CH_3); IR ν (plate 1, neat, cm^{-1}) 2245 (CN), 1088 (SO), 698 (*cis*-HC=CH); EIMS (70 eV) *m/z* 298 [(M - SO)$^+$, 100%]; HRMS (*m/z*) Cald for $C_{20}H_{30}N_2ONaS$ $(M + Na)^+$ 369.1977, found 369.1984.

3,6-Dihexylphthalonitrile (21a). $BF_3.OEt_2$ (3 mL, 24.3 mmol, 6.2 eq.) was added to a heated (30 °C) solution of 2,5-dihexylthiophene (**23a**) (0.99 g, 3.9 mmol) and fumaronitrile (0.62 g, 8.0 mmol, 2.0 eq.) in dry DCM (10 mL). The reaction mixture was heated to reflux and a solution of *m*-CPBA (1.38 g, 8.0 mmol, 2.0 eq.) in dry DCM (30 mL) added dropwise over 30 min. Reflux was continued for 1h, whereafter the reaction mixture was allowed to cool to room temperature. Saturated aqueous $NaHCO_3$ (200 mL) was added and stirring continued for 15 min. The organic phase was washed with H_2O (2 x 100 mL) and brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product and *o*-toluic acid (spatula tip) was dissolved in DCE (7 mL) and the solution exposed to microwave irradiation (60 power cycles). Recrystallization (EtOH) afforded 3,6-dihexylphthalonitrile (**21a**) as white needles (0.46 g, 39%): mp 38-40 °C (lit.[26] 38 °C); R*f* 0.34 (Hexanes : Toluene, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$)[26] δ 7.46 (2H, s, H-4,5), 2.84 (4H, t, *J* = 7.9 Hz, H-1'), 1.69 – 1.62 (4H, m, H-2'), 1.41 – 1.33 (4H, m, H-3'), 1.33 – 1.27 (8H, m, H-4',5'), 0.88 (6H, t, *J* = 7.0 Hz, H-6'); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3 (C-3,6), 133.6 (C-4,5), 115.7 (C-1,2), 115.3 (*C*N), 34.5 (C-1'), 31.6 (C-4'/5'), 30.8 (C-2'), 28.9 (C-3'), 22.6 (C-4'/5'), 14.1 (C-6'); IR ν (neat, cm^{-1}) 2230 (CN); EIMS (70 eV) *m/z* 296 (M^+, 11%).

Preparation of metal-free phthalocyanines

Standard cyclotetramerization procedure

Lithium metal (3 eq.) was added to 1-alcohol (4 mL/mmol) and the solution heated to 140 °C until no solid lithium could be observed. Appropriately substituted solid phthalonitrile was added and heating continued for another 4 h. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (40 mL/mmol). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (20 mL/mmol), H_2O (20 mL/mmol), saturated aqueous $NaHCO_3$ (2 x 20 mL/mmol) and brine (20 mL/mmol). The organic phase was dried over Na_2SO_4 and evaporated to dryness.

1,4,8,11.15,18,22,25-Octaoctyloxyphthalocyanine (27a). Lithium metal (0.11 g, 16.0 mmol, 3.0 eq.) was added to 1-octanol (20 mL) and the solution heated to 140 °C until no solid lithium could be observed. 3,6-Dioctyloxyphthalonitrile (**4a**) (2.01 g, 5.2 mmol) was added and heating continued for another 4 h. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (200 mL). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (200 mL), H_2O (200 mL), saturated aqueous $NaHCO_3$ (200 mL) and brine (200 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. Flash column chromatography (Hexanes : acetone : py 8:1:1) afforded 1,4,8,11.15,18,22,25-octaoctyloxyphthalocyanine (**27a**) as a dark green solid (0.95 g, 47%) : R*f* (Hexanes : Acetone:Py, 8:1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (8H, s, H-p), 4.85 (16H, t, *J* = 7.5 Hz, H-1'), 2.30 – 2.23 (16H, m, H-2'), 1.67 – 1.60 (16H, m, H-3'), 1.51 – 1.45 (16H, m, H-4'), 1.39 – 1.34 (16H, m, H-5'), 1.32 – 1.26 (32H, m, H-6',7'), 0.87 (24H, t, *J* = 7.0 Hz, H-8'), 0.28 (2H, br. s, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2 (C-np), 149.6, 126.6, 117.2 (C-p), 71.6 (C-1'), 32.0, 29.8, 29.6, 29.5, 26.3, 22.8, 14.2 (C-8'); IR[8] ν (neat, cm^{-1}) 3296 (NH); MALDI (*m/z*) 1540 (M^+); UV[8] (toluene) λ_{max}, nm (10^{-4} ε, $L.mol^{-1}.cm^{-1}$) 767 (10.89), 744 (9.22), 334 (4.59).

1,4,8,11.15,18,22,25-Octapentoxyphthalocyanine (27b). Lithium metal (0.03 g, 4.3 mmol, 2.9 eq.) was added to 1-pentanol (5 mL) and the solution heated to 140 °C until no solid lithium could be observed. 3,6-Dipentoxyphthalonitrile (**4b**) (0.45 g, 1.5 mmol) was added and heating continued for another 45 min. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (160 mL). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (160 mL), H_2O (160 mL), saturated aqueous $NaHCO_3$ (160 mL) and brine (160 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. Trituration (DCM : CH_3CN 1:20) afforded 1,4,8,11.15,18,22,25-octapentoxyphthalocyanine (**27b**) as a dark green amorphous solid (0.25 g, 56%): R*f* 1.00 (Py : Toluene: $CHCl_3$, 7:2:1); ^{1}H NMR[45] (600 MHz $CDCl_3$) δ 7.58 (8H, s, H-p), 4.83 (16H, t, *J* = 7.78 Hz, H-1'), 2.31-2.20 (16H, m, H-2'), 1.63-1.55 (16H, m, H-3'), 1.53-1.46 (16H, m, H-4'), 0.97 (24H, t, *J* = 7.30 Hz, H-5'), 0.23 (2H, br. s, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2 (C-np), 126.6 (C-p), 117.1, 71.6 (C-1'), 29.3 (C-2'), 28.4 (C-3'), 22.9 (C-4'), 14.3 (C-5'); IR[45] ν (neat, cm^{-1}) 3286 (NH); MALDI (*m/z*) 1203 (M^+); UV[Error! Bookmark not defined.] (toluene) λ_{max}, nm (10^{-4} ε, $L.mol^{-1}.cm^{-1}$) 762 (13.55), 738 (10.22), 334 (4.86).

1,4,8,11.15,18,22,25-Octabutoxyphthalocyanine (27c). Lithium metal (0.13 g, 18.1 mmol, 3.3 eq.) was added to 1-butanol (15 mL) and the solution heated to 140 °C until no solid lithium could be observed. 3,6-Dibutoxyphthalonitrile (**4c**) (1.50 g, 5.5 mmol) was added and heating continued for 6 h. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (800 mL). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (800 mL), H_2O (800 mL), saturated aqueous $NaHCO_3$ (800 mL) and brine (800 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. Trituration (DCM : CH_3CN 1:20) afforded 1,4,8,11.15,18,22,25-octabutoxyphthalocyanine (**27c**) as a dark green amorphous solid (0.25 g, 56%) : R*f* 0.37 (Hexanes : Acetone : Py, 8:1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (8H, s, H-p), 4.86 (16H, t, *J* = 7.5 Hz, H-1'), 2.29 – 2.19 (16H, , H-2'), 1.71 – 1.62 (16H, m, H-3'), 1.08 (24H, t, *J* = 7.4 Hz, H-4'), 0.28 (2H, br. s, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2 (C-np), 126.6, 117.2 (C-p), 71.3 (C-1'), 31.6 (C-2'), 19.5 (C-3'), 14.2 (C-4'); IR[8] ν (neat, cm^{-1}) 3298 (NH); MALDI (*m/z*) 1093 [$(M+H)^+$]; UV[8] (toluene) λ_{max}, nm (10^{-4} ε, $L.mol^{-1}.cm^{-1}$) 767 (14.11), 741(12.33), 333 (5.71).

1,4,8,11.15,18,22,25-Octahexylphthalocyanine (27d). Lithium metal (0.01 g, 2.0 mmol, 2.9 eq.) was added to 1-pentanol (2 mL) and the solution heated to 140 °C until no solid lithium could be observed. 3,6-Dihexylphthalonitrile (**4d**) (0.20 g, 0.7 mmol) was added and heating continued for 8 h. The reaction mixture was then cooled to ambient temperature, diluted with acetone (30 mL) and the precipitate removed by filtration. The filtrate was acidified with acetic acid (100 mL) and the formed precipitate collected to afford 1,4,8,11.15,18,22,25-octahexylphthalocyanine (**27d**) as a dark green solid (0.07 g, 34%): ^{1}H NMR[26] (600 MHz, $CDCl_3$) δ 7.77 (8H, s, H-p), 4.34 (18H, t, *J* = 7.4 Hz, H-1'), 2.07 – 2.00 (16H, m, H-2'), 1.58 – 1.51 (16H, m, H-3'), 1.36 – 1.24 (32H, m, H-4',5'), 0.84 (24H, t, *J* = 7.2 Hz, H-6'), -0.25 (2H, br. s, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.8, 133.7, 130.6 (C-p), 32.8 (C-1'), 32.3 (C-4'), 30.6 (C-2'), 29.3 (C-3'), 22.8 (C-5'), 14.2 (C6'); IR ν (neat, cm^{-1}) 3302 (NH); MALDI (*m/z*) 1186 (M^+); UV[26] (toluene) λ_{max}, nm (10^{-4} ε, $L.mol^{-1}.cm^{-1}$) 733 (11.97), 699 (10.15), 363 (4.89).

2,3,9,10,16,17,23,24-Octahexylphthalocyanine (28a). Lithium metal (0.01 g, 2.0 mmol, 3.3 eq.) was added to 1-pentanol (2 mL) and the solution heated to 140 °C until no solid lithium could be observed. 4,5-Dihexylphthalonitrile (**16d**) (0.18 g, 0.6 mmol) was added and heating continued for 8 h. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (40 mL). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (40 mL), H_2O (40 mL), saturated aqueous $NaHCO_3$ (40 mL) and brine (40 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. Trituration (DCM : CH_3CN 1:20) afforded 2,3,9,10,16,17,23,24-octahexylphthalocyanine (**28a**) as a dark green solid (0.07 g, 37%): ^{1}H NMR (600 MHz, $CDCl_3$, 323 K) δ 9.00 (8H, s, H-np), 3.19 (16H, br. t, *J* = 8.29 Hz, H-1'), 2.09 – 2.02 (16H, m, H-2'), 1.76 – 1.69 (16H, m, H-3'), 1.61 – 1.49 (32H, m, H-4',5'), 1.04 (24H, t, *J* = 7.3 Hz, H-6'), -1.00 (2H, br. s, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 323 K) δ 143.4, 122.9, 34.3, 32.2, 32.0, 30.2, 23.0, 22.8, 14.3, 14.1; IR[20] ν (neat, cm^{-1}) 3287 (NH); MALDI[Error! Bookmark not defined.] (*m/z*) 1187 (M^+); UV[20] (toluene) λ_{max}, nm (10^{-4} ε, $L.mol^{-1}.cm^{-1}$) 706 (5.2), 670 (4.4), 651 (1.4), 641 (1.3), 608 (0.8), 349 (2.2).

2,3,9,10,16,17,23,24-Octapentoxyphthalocyanine (28b). Lithium metal (0.10 g, 14.28 mmol, 10 eq.) was added to 1-pentanol (15 mL) and the solution heated to 140 °C until no solid lithium could be observed. 4,5-Dipentoxyphthalonitrile (**6c**) (1.52 g, 1.26 mmol) was added and heating continued for 8 h. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (40 mL). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (40 mL), H_2O (40 mL), saturated aqueous $NaHCO_3$ (40 mL) and brine (40 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. Trituration (DCM : MeOH 1:20) afforded 2,3,9,10,16,17,23,24-octapentoxyphthalocyanine (**28b**) as a dark green solid (0.86 g, 57%): R*f* 0.74 (DCM); ^{1}H NMR[45] (600 MHz, $CDCl_3$) δ 8.33 (8H, s, H-np), 4.55 (16H, br. t, *J* = 6.2 Hz, H-1'), 2.25 – 2.18 (16H, m, H-2'), 1.85 – 1.79 (16H, m, H-3'), 1.71 – 1.63 (16H, m, H-4'), 1.15 (24H, t, *J* = 7.4 Hz, H-5'), -2.99 (2H, br. s, N*H*); ^{13}C NMR (151 MHz) δ 151.9, 148.2, 130.0, 105.6 (C-np), 69.9 (C-1'), 29.8 (C-2'), 29.0 (C-3'), 23.0 (C-4'), 14.4 (C-5'); IR[45] ν (neat, cm^{-1}) 3287 (NH); MALDI (*m/z*) 1204 (M^+); UV[45] (toluene) λ_{max}, nm (10^{-4} ε, $L.mol^{-1}.cm^{-1}$) 702 (13.0), 664 (10.7) 648 (4.9), 602 (2.5), 420 (3.3), 354 (6.5).

2,3,9,10,16,17,23,24-Octakis(2,4-di-*tert*-butylphenoxy)phthalocyanine (28c). Lithium metal (0.09 g, 12.9 mmol, 2.1 eq.) was added to 1-pentanol (20 mL) and the solution heated to 140 °C until no solid lithium could be observed. 4,5-Bis-(2,4-di-*tert*-butylphenoxy)phthalonitrile (**6b**) (3.00 g, 5.6 mmol) was added and heating continued for another 1 h. The reaction mixture was then cooled to ambient temperature and transferred to acetic acid (200 mL). All solvent was removed *in vacuo* and the crude product dissolved in DCM. The solution was washed with 3M HCl (200 mL), H_2O (200 mL), saturated aqueous $NaHCO_3$ (200 mL) and brine (200 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness. Flash column chromatography (Hexanes : acetone : py 8:1:1) and trituration (EtOAc : EtOH 1:2) afforded 2,3,9,10,16,17,23,24-octakis(2,4-di-*tert*-butylphenoxy)phthalocyanine (**28c**) as a green amorphous solid (1.14 g, 38%): R*f* 1.00 ($CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (8H, s, H-np), 7.51 (8H, d, *J* = 2.2 Hz, H-3'),

7.21 (8H, dd, *J* = 8.5, 2.2 Hz, H-5'), 6.99 (8H, d, *J* = 8.5 Hz, H-6'), 1.49 (72H, s, 2'- C(C*H*$_3$)$_3$, 1.37 (72H, s, 4'- C(C*H*$_3$)$_3$, -0.32 (2H, br. s, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5 (C-2,1'), 151.5 (C-5), 145.6 (C-4'), 139.2 (C-2'), 133.1 (C-4a), 124.5 (C-3'), 124.1 (C-5'), 117.6 (C-6'), 115.0 (C-1), 35.2 (2'- *C*(CH$_3$)$_3$), 34.7 (4'- *C*(CH$_3$)$_3$), 31.8 (4'- C(*C*H$_3$)$_3$), 30.3 (2'-C(*C*H$_3$)$_3$); IR ν (neat, cm^{-1}) 3305 (NH); MALDI (*m/z*) 2148 (M^+); UV (toluene) λ_{max}, nm (10^{-4} ε, L.mol^{-1}. cm^{-1}) 707 (17.5), 672 (15.0), 352 (5.9); Anal. Calcd for $C_{144}H_{178}N_8O_8$; C, 80.48; H, 8.35; N, 5.21. Found: C, 79.87; H, 8.22; N, 5.04.

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Supplementary Material

NMR spectra can be found online in the supplementary material.

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