CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700745

# Oligomeric Cadmium–Phthalocyanine Complexes: Novel Supramolecular Free Radical Structures

**Isabelle Chambrier, Gaye F. White, and Michael J. Cook***[a]

**Abstract:** Certain cadmium-metallated phthalocyanines give rise to EPR active triple-decker sandwich complexes containing two Cd ions and three phthalocyanine (Pc) ligands. These have been shown to form when the ligands bear either eight non-peripheral alkyl or alkenyl substituents or eight peripheral 2-ethylhexyl groups. They can be derived either from three equivalents of a cadmium phthalocyanine precursor or from a 2:1 mixture of a cadmium phthalocyanine (CdPc) and a metal-free phthalocyanine ($H_2Pc$). The mode of their formation has been investigated by a series of "cross" experiments. The results indicate that the triple-decker structures are formed by a self-assembly process. This is deduced from results that show that they can disassemble and reassemble with incorporation of differently substituted ligands derived from either an $H_2Pc$ or CdPc. The reassembled structures in these cross experiments can contain more than one ligand that originated from either the added CdPc or, and more surprisingly, the $H_2Pc$ compound. Mass spectrometry has also established that higher order oligomers can be formed when steric requirements between the alkyl substituents on adjacent rings in the stack are reduced. Thus an isotopic cluster for a $Cd_5Pc_6$ complex has been observed when the eight peripheral substituents are hexyl chains and tetrameric complexes are formed when two different ligands are incorporated within a stack, with one carrying substituents at the peripheral sites and the other bearing substituents at the non-peripheral sites.

**Keywords:** cadmium · mass spectrometry · phthalocyanines · sandwich complexes

## Introduction

Phthalocyanines (Pcs) are man-made macrocycles that play a major role as commercial dyes and pigments.[1] However, they are also recognised, by virtue of their interesting photophysical and electrical properties, to be highly significant "functional materials". Thus specific derivatives are used as charge carriers in photocopiers, as dyes in laser/LED printing and as laser-light absorbers for optical data storage systems such as CD-Rs.[2–5] Others show promise for exploitation in areas, such as solar cells[6] and gas sensors,[7] while photoexcited state properties render them suitable for optical-limiting[8] and as singlet-oxygen photosensitizers for water purification[9] and photodynamic therapy (PDT).[10]

This range of applications arises from the ease of introducing or tuning specific properties through the incorporation of up to 70 different metallic or metalloid elements into the central cavity of the macrocyclic ligand ($Pc^{2-}$) and through introduction of substituents onto the ring system. Common metallated derivatives include dilithium phthalocyanine [$Li_2Pc$] and 1:1 complexes of the ligand with $M^{II}$ metals to form [$M^{II}Pc$] complexes. Incorporation of trivalent metal ions, for example, $Al^{III}$ or $In^{III}$, leads to metallated Pcs bearing an axial ligand. Valencies of $M^{III}$ ions are also satisfied within triple-decker sandwich complexes, [$M_2Pc_3$], but examples, which include derivatives of lanthanide(III),[11] indium(III)[12] and bismuth(III),[13] are few.

An important but small sub-group of Pcs are those in which the formal charge(s) of the ligand do not match those of the normal valencies of the metal ions, resulting in free-radical derivatives. These compounds are especially promising in the fields of molecular electronics and sensor development.[14] Structure-wise, the simplest example is monolithium phthalocyanine [LiPc], formed by chemical,[15,16] electrochemical[15,17] or photochemical[15] oxidation of [$Li_2Pc$]. It is an unexpectedly stable radical and one of the rare intrinsic organic semiconductors.[18] The second class of radical phthalocyanine are bisphthalocyanines, [$M^{III}Pc_2$], formed most notably from the lanthanides[19–22] and indium.[23] Undoped single crystals of [$LuPc_2$] show significant room-tem-

---

[a] Dr. I. Chambrier, Dr. G. F. White, Prof. M. J. Cook
School of Chemical Sciences and Pharmacy
University of East Anglia, Norwich NR4 7TJ (UK)
Fax: (+44) 1603-592-011
E-mail: m.cook@uea.ac.uk

perature conductivity[18] and, along with other lanthanide bisphthalocyanines, exhibit electrochromism arising from one-electron transfers between readily accessible redox states.[24]

In a recent communication we isolated the first example of a new class of phthalocyanine derivative, **1a**,[25] Figure 1.

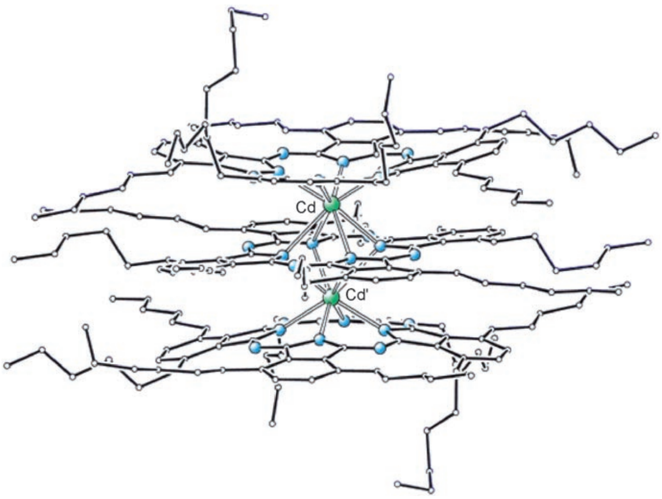


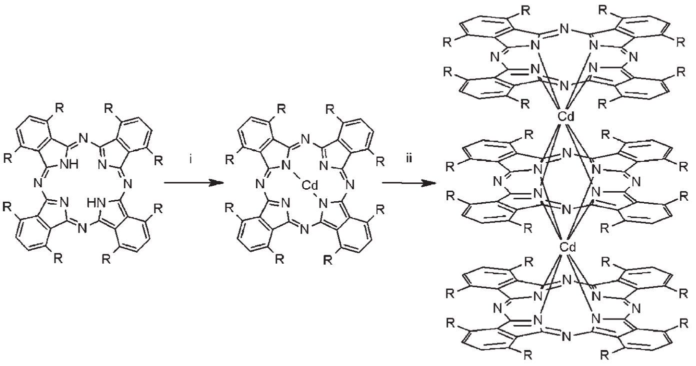
Figure 1. X-Ray structure of **1a**.[25]

The compound combines the triple-decker architecture referred to above but with a metal(II) ion, in this case cadmium. The complex, in which there is a formal charge imbalance between the three $Pc^{2-}$ ligands and two $Cd^{2+}$ ions, exhibits a remarkable set of redox states; it is also EPR active with signal intensity in $CH_2Cl_2$ indicating the presence of less than one molar equivalent of a radical species. The cyclic voltammogram of the material in $CH_2Cl_2$ provides evidence of six one-electron oxidation and twelve one-electron reduction processes, which, in view of the redox inactivity of cadmium, are attributed to ring-based processes. The finding that **1a** in the rest state can undergo six ring-based one-electron oxidations implies each ligand is indeed in the $Pc^{2-}$ state. Thus the species in the neutral state can be regarded as having the general structure $[H]_2[Cd_2Pc_3]$, in which "$[H]_2$" refers to protons serving as counterions. The first one-electron oxidation from this spin 0 state occurs at $E^{o\prime} = 0.162$ V, much lower than is typical of simple Pc derivatives, and could account for the presence of amounts of an oxidised, spin 1/2 species, leading to the EPR signal.

The present paper reports conditions that favour the formation of this new class of material, the development of this novel chemistry through synthesis of analogues, the investigation of the self-assembling processes involved in generating these triple-decker complexes and the detection of higher oligomers.

## Results and Discussion

**First isolation of compound 1a and characterisation data**: There are very few reports on cadmium phthalocyanines in the literature[26] although the unsubstituted 1:1 cadmium phthalocyanine complex is available from a commercial source. The first indications of the formation of the triple-decker sandwich complex **1a** arose from a reaction expected to convert the metal-free derivative **2a**, a compound substituted with eight hexyl chains at the non-peripheral 1,4,8,11,15,18,22,25-sites on the ring system, into the corresponding substituted cadmium phthalocyanine derivative **3a** (Scheme 1). Though the isolation of pure **3a** was satisfactorily achieved (see next section), it was not without initial difficulties because of frequent contamination with either the metal-free precursor **2a** or a dark blue material that ultimately proved to be **1a**.



| | | | |
|---|---|---|---|
| **2a** | R=$n$-$C_6H_{13}$ | **3a** | **1a** |
| **2b** | R=$n$-$C_8H_{17}$ | **3b** | **1b** |
| **2c** | R=$n$-$C_{10}H_{21}$ | **3c** | **1c** |
| **2d** | R=$(CH_2)_6CH{=}CH_2$ | **3d** | **1d** |
| **2e** | R=$OC_6H_{13}$ | | |
| **2f** | R=$CH_2O(CH_2)_5CH_3$ | | |

Scheme 1. Synthesis of **1a**–**1d**. Reagents: i) $Cd(OAc)_2$, pentanol; ii) recrystallisation $CH_2Cl_2$/methanol.

Thus an attempt to separate **3a** from the crude reaction product by column chromatography over silica gel led to both **3a** and a fraction that proved to be the starting material **2a**. The latter arose apparently through de-metalation of **3a** on the column. When neutral alumina was used as the stationary phase a minor dark blue fraction was eluted prior to **3a**. The blue material also appeared as a contaminant of **3a** during preliminary recrystallisation attempts. Furthermore, a green solution of **3a** in chloroform very slowly changed colour to dark blue on standing. The dark blue compound was subsequently obtained pure when it crystallised out unexpectedly during attempted slow recrystallisations of **3a** from either THF/MeOH or $CH_2Cl_2$/MeOH; its structure, Figure 1, was identified as **1a** by X-ray crystallography.[25]

The UV/Vis spectra of **3a** in hexane and **1a** in various solvents are shown as Figure 2. The former gives rise to the strong Q-band absorption at 708 nm that is characteristic of a metallated phthalocyanine substituted with alkyl chains. However, the spectrum of **1a** is more complex with electronic absorptions at 867, 718, 646, 599 and 483 nm (in hexane); the relative intensities of some of these bands vary

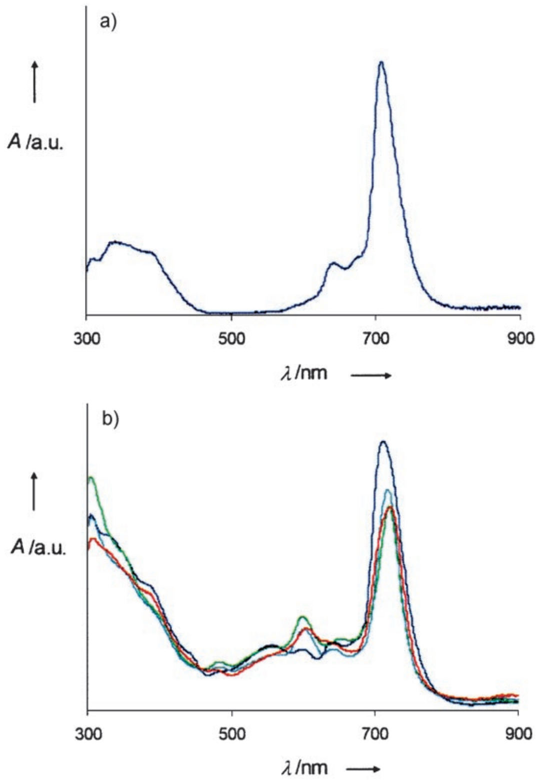


Figure 2. a) UV/Vis spectrum of **3a** in hexane; b) UV/Vis spectra of **1a** in THF (dark blue), toluene (light blue), $CH_2Cl_2$ (red) and hexane (green) at the same concentration (15 μM).

somewhat in other solvents, for example, THF and toluene, Figure 2b. The EPR activity of **1a**, which was referred to above, and the intensity of the radical signal also shows some solvent dependency. Measurement of signal intensity relative to that from a known concentration of a standard spin label [(1-oxyl-2,2,5,5-tetramethyl-[D]-pyrroline-3-methyl)methanethiosulfonate; MTSL], showed the radical content, that is, mole fraction of radical, to vary as follows: THF 0.18 ($g=1.9934$), toluene 0.45 ($g=1.9952$) and hexane 0.36 ($g=1.9938$). We surmise that both the variation in absorption intensities of specific UV/Vis bands and radical content arise from solvent-induced perturbation of the equilibrium between spin 0 and spin 1/2 species referred to earlier.

The presence of a paramagnetic species accounts for line broadening that is observed in the $^1H$ NMR spectrum of **1a**. The spectrum measured of a solution of **1a** in [$D_6$]benzene showed very broad and/or unresolvable NMR signals; that measured in [$D_3$]chloroform was somewhat better resolved and showed a broad signal for the aromatic protons. However, there are no detectable signals in the "benzylic region" of the spectrum; the most downfield of the non-aromatic proton signals appear at 2.65 ppm. The MALDI-TOF mass spectrum of **1a** shows peaks that can be assigned to fragmentation of the molecular ion, which itself is not detected (isotopic clusters at 2598.7 [$Cd_2Pc_2$]; 2484.8, [$CdPc_2$], 1299.1-[CdPc] and 1187.1 [$H_2Pc$]).

**Optimised conditions for the synthesis of 1a**: A reproducible protocol for obtaining **1a** was first sought based on Scheme 1, with the twin objectives of optimising the isolation of pure **3a** and establishing conditions for its conversion into the triple-decker sandwich complex. The first was achieved by reacting the metal-free compound, **2a**, in refluxing pentanol with a twofold excess of cadmium acetate, with reflux maintained for 45 minutes. The hot solution was added to cold methanol and the mixture left at 4 °C overnight. The green precipitate was collected and washed with MeOH, and the cadmium-metallated compound, **3a**, was separated from excess cadmium acetate by dissolving it into THF. Rapid addition of excess MeOH to the solution re-precipitated **3a** as pure material, uncontaminated by **1a**, and was characterised by elemental analysis, MALDI-TOF mass spectrometry and NMR spectroscopy.

A protocol for converting **3a** into **1a** was developed that involved dissolving **3a** in dichloromethane containing a few drops of MeOH. The solution slowly turned blue over a period of 15 h at 4 °C. UV/Vis spectroscopic monitoring over this period showed the gradual formation of **1a**. Compound **1a** crystallised out upon addition of further methanol in 73 % yield. Parallel experiments demonstrated the importance of the addition of the first few drops of MeOH to the solution of **3a** in dichloromethane. Excess methanol merely precipitated **3a** from solution; with no methanol added, peaks corresponding to the formation of the triple-decker **1a** were not detected by UV/Vis spectroscopy over 24 h. The fate of the displaced cadmium ion during the conversion of **3a** into **1a** is uncertain. We saw no evidence for precipitated material that could point to the formation of cadmium metal or cadmium oxide and we postulate that it may be taken up as cadmium methoxide.

In a variant of the protocol for obtaining **1a**, the same procedure was applied to a solution (in $CH_2Cl_2$/MeOH) containing the two formal components of the triple-decker sandwich compound, that is, two equivalents of **3a** and one equivalent of the metal-free analogue, **2a**. This mixture indeed provided an alternative access to **1a**, which was isolated in 76 % yield, comparable to that obtained from **3a** alone. This result establishes that a metal-free Pc can participate in the formation of the triple-decker sandwich complex, a result which is explored further later in this paper.

In a separate experiment, an attempt was made to obtain **1a** directly from the metal-free compound **2a** by using a fivefold excess of cadmium acetate. The reaction yielded a blue powder, but this proved not to be **1a**. The UV/Vis spectrum showed a broad absorption peak at 721 nm and the product gave a $^1H$ NMR spectrum in [$D_6$]benzene that did not show peak broadening of the kind observed in the spectrum of **1a**. The NMR spectrum is complex but well resolved, Figure 3. The signals are tentatively assigned to a triple-decker sandwich complex, but capped with cadmium monoacetate at both ends (structure **4**). Two aromatic singlets at 7.96 and 8.65 ppm integrate for 16 H and 8 H, respectively, and there are signals at 4.31, 3.54 and 3.30 ppm each integrating for 16 H and correspond to the benzylic

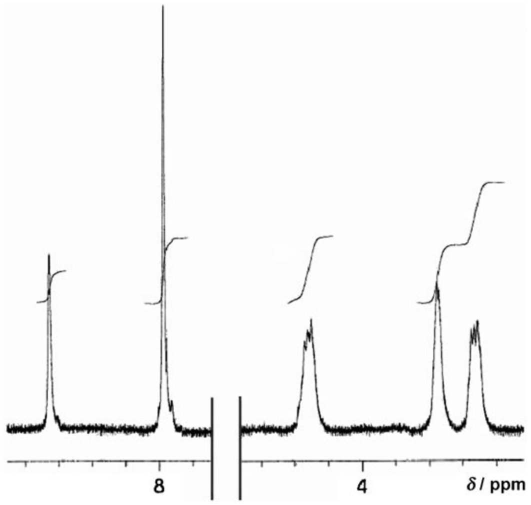
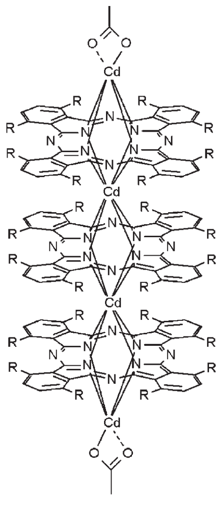


Figure 3. Aromatic and benzylic regions of the $^{1}$H NMR spectrum of **4** measured in [D$_6$]benzene.



**4**

protons. The protons giving rise to the signals at 4.31 and 3.30 ppm are coupled (COSY) and are assigned to the two sets of diastereotopic protons that arise from the non-equivalence of the two faces of the outer Pc ligands. The signal at 3.54 ppm is then assigned to the benzylic protons of the inner Pc ring. In [D$_3$]chloroform, a signal at $-0.82$ ppm, integrating for 6H, was also apparent and is tentatively assigned to the acetate groups of the CdOAc-capping moieties. The closest reported structural analogue to that proposed above which we are aware of is a polymeric Pc complex in which the rings are linked by Hg$^{2+}$ ions with the terminal rings capped by Hg$^{II}$ monoacetate units.[27]

Unfortunately, it proved impossible to isolate the new oligomeric complex, **4**. All attempts to remove the excess cadmium acetate used in the reaction led to decomposition of the product. When a solution of the product was left in dichloromethane for a few hours, the absorption spectrum slowly developed the characteristics of the UV/Vis spectrum of **1a**. However, we did not seek to develop this finding as an alternative protocol for the synthesis of **1a**.

## Syntheses and attempted syntheses of homologues and analogues of 1a

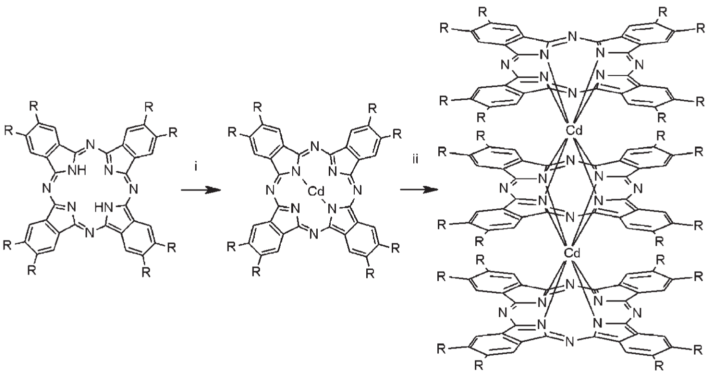
*Non-peripherally octasubstituted derivatives*: Cadmium insertion into metal-free 1,4,8,11,15,18,22,25-octakis(octyl)-, octakis(decyl)- and octakis(octenyl)phthalocyanines (**2b**, **2c** and **2d**, respectively) was achieved satisfactorily to give the corresponding non-peripherally substituted cadmium-phthalocyanine complexes, **3b, 3c** and **3d**. However, attempts to metallate the corresponding hexyloxy and hexyloxymethyl derivatives, **2e** and **2f**, with cadmium acetate gave red derivatives that were insoluble in common organic solvents. Cadmium is known to have an affinity for oxygenated compounds and at this time we have not attempted to identify the chemistry involved in these reactions.

The three new cadmium-phthalocyanine complexes **3b–d** were successfully converted into triple-decker sandwich compounds, **1b–d**, respectively, in good yields either by allowing them to stand alone or to self-assemble with an appropriate amount of the metal-free analogue under the two sets of conditions reported above for the formation of **1a**. Evidence for their formation followed from their UV/Vis spectra, which were superimposable on that for **1a**, satisfactory elemental analysis data and MALDI-TOF spectral data, which showed fragmentation peaks that corresponded to those observed for the fragmentation of the molecular ion of **1a**. Though the resolution of the $^{1}$H NMR signals for the aromatic and benzylic protons suffered from the presence of a paramagnetic species, the spectrum of **1d** clearly showed two sets of signals (ratio 2:1) arising from the protons attached to the terminal alkene units. These protons are evidently too distant from the core of the molecule to experience the paramagnetism of the free radical.

*Peripherally octasubstituted derivatives*: Phthalocyanine derivatives with substituents at the 2,3,9,10,16,17,23,24 (or peripheral) sites differ from those bearing comparable substituents at the non-peripheral sites in that they generally show lower solubility and a greater tendency to aggregate in solution. This presumably reflects the fact that the substituent chains are better accommodated broadly within the plane containing the Pc nucleus: X-ray structural determinations of non-peripherally octaalkyl-substituted compounds show that at least two alkyl chains are forced out of the plane and lie approximately orthogonal to the ring plane.[28] Accordingly, the location of the substituents at the peripheral sites could experience lower steric strain within sandwich-type structures.

Two Pc ligands bearing eight alkyl chains at the peripheral sites were selected for investigation, one with 2-ethylhexyl substituents and the other with less bulky *n*-hexyl chains. Thus the metal-free derivatives **5a** and **5b** were converted into the corresponding cadmium phthalocyanines, **6a** and **6b**, Scheme 2. These were satisfactorily characterised and showed Q-bands at 686 and 688 nm, respectively, that is, to the blue of the corresponding band exhibited by compounds **3a–d**, and to be expected as a consequence of the different locations of the substituents.[29]

As was found for the cadmium phthalocyanine derivatives **3a–3d**, a solution of **6a** in dichloromethane turned blue on addition of methanol and a new compound crystallised out as microcrystals. The UV/Vis spectrum of this compound, Figure 4a, showed a complex band structure a little different from that exhibited by compounds **1a–d**. Its $^{1}$H NMR spec-



**5a** R=2-ethylhexyl **6a** **7a**
**5b** R=$n$-$C_6H_{13}$ **6b**

Scheme 2. Synthesis of peripherally substituted derivatives. Reagents: i) $Cd(OAc)_2$, pentanol; ii) recrystallisation $CH_2Cl_2$/methanol.

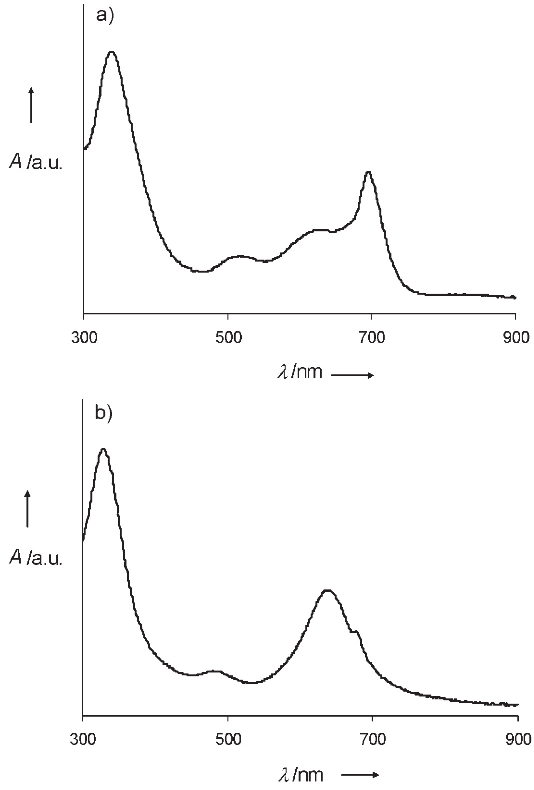


Figure 4. a) UV/Vis spectrum of **7a**; b) UV/Vis spectrum of the product resulting from the recrystallisation of **6b** using the dichloromethane/MeOH procedure.

trum was poorly resolved; the EPR spectrum (hexane as solvent) showed qualitatively a signal at $g = 1.9985$. The compound was assigned structure **7a** on the basis of elemental analysis and the MALDI-TOF mass spectrum. Unlike the spectra of **1a–d**, compound **7a** gave an isotopic cluster (100%) corresponding to a $[Cd_2Pc_3]$ structure. There was no evidence, however, for additional protons in the mass spectrum; we note that the "balancing proton" in the blue form of lutetium bis-phthalocyanine, usually denoted as either $[LuH(Pc)_2]$ or $H[Lu(Pc)_2]$, has also proved difficult to detect.[11] The spectrum of **7a** included fragmentation peaks corresponding to $[Cd_2Pc_2]$ and [CdPc].

A solution of the second peripherally substituted cadmium phthalocyanine **6b** in dichloromethane also gave a dark blue precipitate when treated with methanol, as above. However, the UV/Vis spectrum differed from that exhibited by **7a**, Figure 4b, implying the formation of an alternative type of sandwich compound. This was confirmed by the MALDI-TOF mass spectrum, which showed a remarkably complex series of signals, Figure 5. The highest molecular weight species, $m/z$ 7676.7, corresponds to a structure with six ligands and five cadmium ions; there are also peaks that correspond to lower oligomers. Whether these signals correspond to fragmentation peaks or to more than one species in the recovered product is uncertain. Elemental analysis did not clarify the situation other than to show that a $[Cd_5Pc_6]$ structure alone would not account for the experimentally determined C, H, and N content. A solution of the product in $n$-hexane gave rise to an EPR signal.

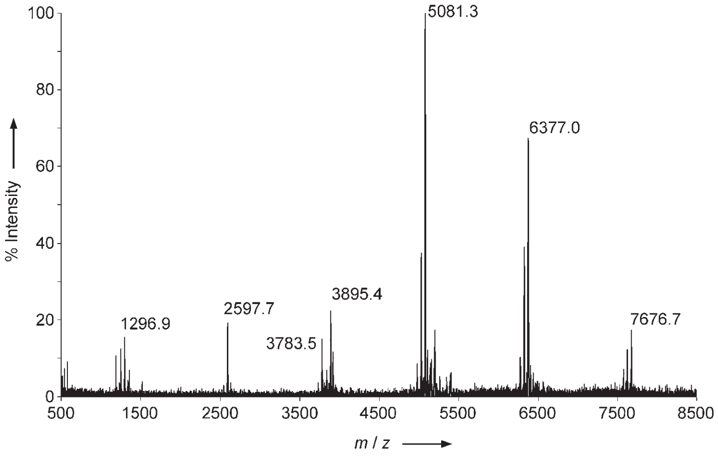
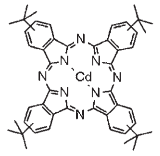


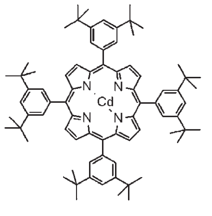
Figure 5. MALDI mass spectrum of the product resulting from the recrystallisation of **6b** from dichloromethane/MeOH. The 7676.7 cluster corresponds to a $Cd_5Pc_6$ complex, the 6377.0 cluster to a $Cd_4Pc_5$ complex, the 5081.3 cluster to a $Cd_3Pc_4$ complex, the 3895.4 to a $Cd_3Pc_3$ complex and the 3783.5 cluster to a $Cd_2Pc_3$ complex.

The formation of structures more complex than a triple-decker sandwich when the Pc ligand bears less spatially demanding groups, that is, hexyl chains, implies that the extent of steric interactions between adjacent ligands in a stack may be a controlling factor in the oligomerisation process.

*Other analogues*: Metallated tetra-*tert*-butylphthalocyanines have been much studied as readily accessible derivatives soluble in organic solvent and accordingly we investigated the hitherto unknown cadmium derivative **8**. This was prepared from the metal-free analogue by the usual procedure, but it proved to have unexpectedly low solubility in chloroform and methylene chloride, so hindering attempts to convert this into a triple-decker sandwich compound.



8



9

We also undertook a brief investigation into the potential for converting a cadmium porphyrin derivative into a sandwich complex, focussing on the tetrakis(3,5-di-*tert*-butylphenyl)porphyrin ligand. The metal-free analogue was converted into the cadmium derivative **9**, which proved to have satisfactory solubility in chloroform and dichloromethane to apply the conditions that promoted formation of phthalocyanine triple-decker complexes. However, these conditions failed to induce a change in the UV/Vis spectrum of **9** over several days.

In the light of these investigations it appears that the formation of oligomeric cadmium phthalocyanines may be restricted to certain specifically substituted phthalocyanine ligands.

**Mixed precursor experiments—probes for understanding oligomer formation**: A variety of experiments were undertaken involving two differently substituted cadmium phthalocyanines, referred to as CdPc and CdPc′, and unsurprisingly the triple-decker complexes formed from these gave mass spectral data consistent with the incorporation of both precursors. Typical evidence from experiments with two different non-peripherally substituted compounds were fragmentation peaks corresponding to Pc-Cd-Pc′ species.

In light of the formation of **1a** from a solution containing two equivalents of the substituted cadmium phthalocyanine **3a** and one equivalent of the metal-free analogue **2a**, vide supra, we undertook further mixed precursor experiments to investigate the mode of formation of triple-decker complexes by this protocol. These experiments, exemplified by entries 1 and 2 in Table 1, were undertaken by dissolving two equivalents of a substituted CdPc and one equivalent of a differently substituted metal-free phthalocyanine, denoted as $H_2Pc'$, in dichloromethane as solvent, to which were added two drops of methanol. Further methanol was added after 15 h to precipitate out oligomeric complexes that had been formed in the solution.

Experiment 1 was undertaken with **3a** as the CdPc component and **2d** as the $H_2Pc'$ component, the alkenyl protons of the latter offering a probe for readily establishing its incorporation into a triple-decker structure. The $^1$H NMR spectrum of the triple-decker complex(es) in the product mixture indeed showed signals for terminal alkenyl protons; moreover it showed signals for alkene groups in two different environments in a ratio of 2:1. This demonstrated that the ligand of the metal-free complex **2d** had not only been incorporated into the triple-decker complex, but also shows that it is incorporated at both the outer and inner sites. This result is significant with regard to the formation of triple-decker complexes from 2:1 mixtures of a CdPc and an $H_2Pc$. In particular, it precludes a mechanism by which the metal-free complex merely serves to "cap" an intermediate dimeric structure of the type $Cd_2Pc_2$. As expected from the previous results for non-peripherally substituted complexes, the MALDI-TOF spectrum did not show molecular ions, but showed peaks assignable to the fragment ions containing both Pc-Cd-Pc and Pc-Cd-Pc′ moieties.

Experiment 2, utilising **3a** as the CdPc component and **5a** as the $H_2Pc'$, provided further insight. The MALDI-TOF spectrum of the precipitated complexes showed at higher mass numbers evidence for structure(s) containing four ligands: two non-peripherally substituted ones from the CdPc compound and two peripherally substituted ones arising from the $H_2Pc'$ compound. The sequence of the ligands in this "2:2" tetrameric stack cannot, of course, be surmised from the mass spectrum. However, the formation of a tetrameric structure containing ligands that, alone, give rise only to triple-decker complexes (**1a** and **7a**) can be rationalised in terms of reduced steric interactions between adjacent ligands when one is non-peripherally substituted and the other peripherally substituted. The second significant isotopic cluster in the mass spectrum corresponds, remarkably, to a triple-decker complex (**7a**) containing exclusively the ligands from the $H_2Pc'$ compound.

These results, showing the formation of multi-ligand complexes derived either in part or in whole from a metal-free compound, require one or more processes whereby at some stage a Cd ion from a CdPc molecule becomes available to link ligands from $H_2Pc'$ molecules. A simple process would involve Cd ion transfer between CdPc and $H_2Pc'$ molecules via an intermediate of the form [Pc-Cd-Pc′·2H] leading ultimately to a scrambling of the Cd ion between the two ligands Pc and Pc′. However, although this process cannot be ruled out, the results of experiments 3–6 suggest an alternative mechanism may prevail that involves triple-decker complexes themselves.

Table 1. Results from mixed experiments.

| Expt No | Component 1 (2 equiv) | Component 2 (1 equiv) | Selected observations re components of the product mixture of oligomers |
|---|---|---|---|
| 1 | CdPc (**3a**) | $H_2Pc'$ (**2d**) | scrambling of ligand from **2d** into a triple-decker structure ($^1$H NMR) |
| 2 | CdPc (**3a**) | $H_2Pc'$ (**5a**) | formation of '2:2 tetramers' with two ligands derived from both **3a** and **5a** |
| 3 | $Cd_2Pc_3$ (**1a**) | $H_2Pc'$ (**5a**) | incorporation of ligand from **5a** into oligomer |
| 4 | $Cd_2Pc_3$ (**1a**) | CdPc′ (**6a**) | incorporation of ligand from **6a** into oligomer |
| 5 | $Cd_2Pc_3$ (**7a**) | $H_2Pc'$ (**2a**) | evidence of formation of '2:2 tetramers' |
| 6 | $Cd_2Pc_3$ (**7a**) | CdPc′ (**3a**) | fragmentation peak corresponding to Pc-Cd-Pc′ |

These experiments explored the effect of mixing a preformed triple-decker complex, $Cd_2Pc_3$, with a differently substituted $H_2Pc'$ or $CdPc'$ in $CH_2Cl_2$/MeOH. Experiments 3 and 4 involved the triple-decker **1a** admixed with, separately, **5a** and **6a** and precipitating the components of the mixture by addition of excess MeOH after 24 h. The mass spectrum of the mixture from experiment 3 is shown in Figure 6.

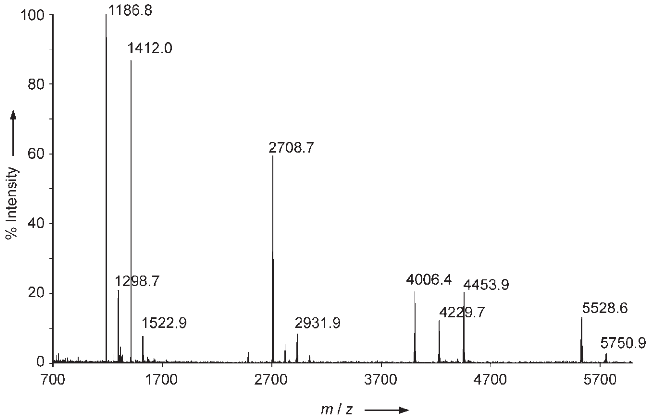


Figure 6. MALDI mass spectrum of the mixture from experiment 3. The 5750.9 cluster corresponds to a $Cd_3Pc'_3Pc$ complex, the 5528.6 cluster to a $Cd_3Pc'_2Pc_2$ complex, the 4453.9 cluster to a $Cd_2Pc'_3$ complex, the 4229.7 cluster to a $Cd_3Pc'Pc_2$ complex, the 4006.4 cluster to a $Cd_2Pc_2Pc'$ complex, the 2932.9 cluster to a $CdPc'_2$ complex and the 2708.7 cluster to a $CdPcPc'$ complex (see Table 1).

It is very similar to that obtained from experiment 2. Thus it shows the presence of the triple-decker containing all three ligands from the metal-free compound. In addition there are isotopic clusters corresponding to the 2:2 tetramers, referred to above, and to 1:3 tetramers containing one ligand from the starting $Cd_2Pc_3$ complex **1a** and three from the added metal-free compound. The mass spectrum of the product from experiment 4 was also complex and included a cluster corresponding to a mixed triple-decker.

Experiments 5 and 6 were undertaken for comparative purposes from the triple-decker **7a** admixed with the $H_2Pc'$ or $CdPc'$ compounds, **2a** and **3a**, respectively. The mass spectrum of the precipitate from experiment 5 included a cluster for the 2:2 tetramers, while that for experiment 6 included a cluster for a mixed dimer, Pc-Cd-Pc′, presumably as a fragmentation peak.

The results of this series of experiments provide strong evidence that in the solution phase, the triple-decker complexes can disassemble and the components reassemble with inclusion of the added $CdPc'$ or $H_2Pc'$ to generate new mixed triple-deckers.

## Conclusion

Our research has uncovered some novel and unexpected chemistry of cadmium phthalocyanines. Specific cadmium-metallated derivatives give rise to a remarkable type of triple-decker sandwich complex containing two Cd ions and three phthalocyanine ligands. These have been shown to form when the ligands bear either eight non-peripheral alkyl or alkenyl substituents or eight peripheral 2-ethylhexyl groups. The novel triple-decker structures have been fully characterised by elemental analysis and supported by MALDI-TOF mass spectrometry data. The complexes are EPR active and as such add an interesting new sub-class of compound to the already substantial range of known phthalocyanine-based derivatives.

Mass spectrometry has also established that higher order oligomers can be formed when steric requirements between the alkyl substituents on adjacent rings in the stack are reduced. Thus an isotopic cluster for a $Cd_5Pc_6$ complex has been observed when the eight peripheral substituents are hexyl chains and tetrameric complexes are formed when two different ligands are incorporated within a stack, with one carrying substituents at the peripheral sites and the other bearing substituents at the non-peripheral sites.

Investigations of the optimised synthesis of the complexes have focused on the preparation of the triple-decker materials. These can be derived either from three equivalents of a simple cadmium phthalocyanine derivative or from a 2:1 mixture of a cadmium phthalocyanine and a metal-free phthalocyanine. The mode of their formation has been investigated by a series of “cross” experiments. The results indicate that the triple-decker structures are formed by a self-assembly process. This is deduced from results that show that they can disassemble and reassemble with incorporation of differently substituted ligands derived from either an $H_2Pc$ or CdPc. The reassembled structures in these cross experiments can contain more than one ligand that originated from either the added CdPc or, and more surprisingly, the $H_2Pc$ compound.

Ongoing work is now focusing on the investigation of the redox properties of the complexes described herein and the potential applications of the materials in device development. In particular further work is in progress to expand on preliminary findings that **1a** exhibits remarkable temperature- and voltage-dependent semiconductivity.[30]

## Experimental Section

**General**: All solvents were SLR or analytical grade and were used as supplied. Commercially available materials were used without further purification. Infrared spectra were recorded as powders on a Perkin–Elmer Spectrum BX equipped with a DuraSamplIR II ATR attachment. NMR spectra were recorded at 400 MHz for $^1H$ and 75.4 MHz for $^{13}C$ on a Varian Unity plus spectrometer. The residual solvent peak was used as reference (7.15 ppm for [$D_6$]benzene and 7.27 ppm for [$D_3$]chloroform). UV/Vis spectra were recorded on a Hitachi U-3000 spectrophotometer in the solvent stated. Melting points and phase transition temperatures (crystal, K; discotic mesophase, D; isotropic liquid, I) were recorded using an Olympus BH-2 polarising microscope fitted with a Linkham THM 600 hotstage. Microanalysis data were obtained using a Carlo Erda 1106 Elemental Analyzer and are quoted to the nearest 0.01 %. MALDI-TOF mass spectra were recorded using an Applied Biosystems Voyager-DE-STR at the EPSRC National Mass Spectrometry Service Centre at the University of Wales in Swansea (UK), with DCTB (trans-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile) as matrix. EPR measurements were carried out at 295 K on a Bruker E500 continuous wave X-band EPR spectrometer fitted with a Bruker ER4123D dielectric room temperature resonator. (1-Oxyl-2,2,5,5-tetramethyl-[D]-pyrroline-3-methyl)methanethiosulfonate (MTSL) was used as standard.

**Materials**: Metal-free phthalocyanine precursors **2a**, **2b**, **2c**, **2e** and **2f** were available from previous reported work on these compounds.[31–33] The precursor to compound **8** was available from Aldrich. The free-base precursor to compound **9** was prepared by condensation of 3,5-di-*tert*-butylbenzaldehyde and pyrrole.[34] Compound **2d** was prepared from furan using a route first described for the synthesis of a lower saturated homologue.[31]

**1,4,8,11,15,18,22,25-Octakis(hexyl)phthalocyaninatocadmium (3a)**: In a typical experiment, 1,4,8,11,15,18,22,25-octakis(hexyl)phthalocyanine **2a** (500 mg, 0.42 mmol) in pentan-1-ol (20 mL) was brought to reflux. Cadmium acetate hydrate (99.99+%; 2 equiv, excess) was added and reflux was continued for 45 min. The hot mixture was added to excess cold MeOH (150 mL) and the flask left in the fridge overnight. The green solid was filtered and washed with MeOH. The green solid was redissolved in THF and the solution filtered to remove the insoluble cadmium salt residue. The solvent was then removed under reduced pressure and the solid reprecipitated from excess MeOH to yield a green powder (350 mg, 64%). M.p. (DSC transition energies): K–D 131.1 °C (0.75 $\mathrm{J\,g^{-1}}$), D–D 166 °C (1.34 $\mathrm{J\,g^{-1}}$), D–D 192.8 °C (undetected), D–I 244.4 °C (0.19 $\mathrm{J\,g^{-1}}$); $^1$H NMR (400 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta=7.75$ (s, 8H), 4.63 (t, $J=7.2$ Hz, 16H), 2.2 (m, 16H), 1.6 (m, 16H), 1.1–1.3 (m, 32H), 0.75 ppm (t, $J=7.2$ Hz, 24H); $^{13}$C NMR (75.4 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta=155.38$, 138.55, 136.68, 130.21, 33.02, 32.43, 31.3, 29.34, 22.85, 14.05 ppm; IR (neat, ATR): $\tilde{\nu}=$ 2952.61, 2920.92, 2851.56, 1313.26, 1151.81, 1084.52, 883.15 $\mathrm{cm^{-1}}$; UV/Vis (*n*-hexane): $\lambda_{max}=709$, 643 nm; MALDI-MS: isotopic cluster at *m/z* (%): 1298 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{80}H_{112}N_8Cd$: C 74.01, H 8.69, N 8.63; found: C 74.15, H 8.72, N 8.47.

**1,4,8,11,15,18,22,25-Octakis(octyl)phthalocyaninatocadmium (3b)**: The product was prepared as for **3a** from 1,4,8,11,15,18,22,25-octakis(octyl)phthalocyanine **2b** (93%). M.p. K–D 81.8 °C, D–I 212.3 °C; $^1$H NMR (400 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta=7.87$ (s, 8H), 4.83 (t, $J=6.8$ Hz, 16H), 2.35 (quint, $J=7.6$ Hz, 16H), 1.77 (quint, $J=7.6$ Hz, 16H), 1.41 (quint, $J=7.6$ Hz, 16H), 1.26 (quint, $J=6.8$ Hz, 16H), 1.18 (m, 32H), 0.79 ppm (t, $J=7.2$ Hz, 24H); $^{13}$C NMR (75.4 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta=155.32$, 138.55, 136.65, 130.20, 33.0, 32.04, 31.36, 30.2, 29.67, 29.54, 22.72, 13.98 ppm; IR (neat, ATR): $\tilde{\nu}=2952.32$, 2918.76, 2849.34, 1313.65, 1147.39, 1083.31 $\mathrm{cm^{-1}}$; UV/Vis (THF): $\lambda_{max}=707$, 642 nm; MALDI-MS: isotopic clusters at *m/z* (%): 1523.0 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{96}H_{144}N_8Cd$: C 75.73, H 9.53, N 7.36; found: C 76.0, H 9.5, N 7.22.

**1,4,8,11,15,18,22,25-Octakis(decyl)phthalocyaninatocadmium (3c)**: The product was prepared as for **3a** from 1,4,8,11,15,18,22,25-octakis(decyl)phthalocyanine **2c** (94%). M.p. K–D 81.8 °C, D–I 177.9 °C; $^1$H NMR (400 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta=7.87$ (s, 8H), 4.83 (t, $J=6.4$ Hz, 16H), 2.35 (quint, $J=6.4$ Hz, 16H), 1.78 (quint, $J=6.2$ Hz, 16H), 1.43 (quint, $J=6.8$ Hz, 16H), 1.17–1.28 (m, 80H), 0.83 ppm (t, $J=6.8$ Hz, 24H); $^{13}$C NMR (75.4 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta=155.39$, 138.58, 136.69, 130.22, 33.06, 32.03, 31.38, 30.31, 29.95, 29.88, 29.74, 29.51, 22.79, 14.04 ppm; IR (neat, ATR): $\tilde{\nu}=2916.87$, 2848.31, 1465.90, 1314.86, 1147.33, 1084.2 $\mathrm{cm^{-1}}$; UV/Vis (THF): $\lambda_{max}=708$, 641 nm; MALDI-MS: isotopic cluster at *m/z* (%): 1748.3 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{112}H_{176}N_8Cd$: C 76.99, H 10.15, N 6.41; found: C 77.21, H 10.3, N 6.15.

### Tris[1,4,8,11,15,18,22,25-octakis(hexyl)phthalocyaninate]dicadmium (1a)

*Method 1*: In a typical experiment, **3a** (350 mg, 0.27 mmol) was recrystallised thrice from $CH_2Cl_2$/MeOH to afford a dark blue crystalline material (150 mg, 44%). M.p. 220 °C (decomp); IR (neat, ATR): $\tilde{\nu}=2950.75$, 2918.0, 2849.64, 1604.2, 1365.16, 1287.22, 1266.26, 1189.81, 1093.03 $\mathrm{cm^{-1}}$; UV/Vis (*n*-hexane): $\lambda_{max}(\varepsilon)=718$ ($1.3\times10^5$), 599 ($0.6\times10^5\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$), 550, 484 nm; MALDI-MS: isotopic clusters at *m/z* (%): 2598.7 (10) [*M*−Pc]$^+$, 2484.8 (55) [*M*−CdPc]$^+$, 1299.1 (100) [*M*−CdPc$_2$]$^+$, 1187.1 (55) [*M*−Cd$_2$Pc$_2$]$^+$; elemental analysis calcd (%) for $C_{240}H_{336}N_{24}Cd_2$: C 76.17, H 8.95, N 8.88; found: C 76.06, H 8.95, N 8.79.

*Method 2*: Compounds **3a** (45 mg, 34.7 μmol) and **2a** (20.6 mg, 17.3 mmol) were dissolved in dichloromethane (4.5 mL) and five drops of methanol added. The solution was placed at 4 °C for 20 h. After that time more methanol was added to precipitate the dark blue powder (50.2 mg, 77%).

**Tris[1,4,8,11,15,18,22,25-octakis(octyl)phthalocyaninate]dicadmium (1b)**: The product was prepared as for **1a** (method 1) from **3b**. A pure dark blue powder was obtained after one recrystallisation of the crude product from $CH_2Cl_2$/MeOH (80%) M.p. 151 °C (decomp); IR (neat, ATR): $\tilde{\nu}=$ 2915.51, 2846.28, 1604.47, 1365.32, 1299.84, 1271.82, 1189.43, 1097.93 $\mathrm{cm^{-1}}$; UV/Vis (*n*-hexane): $\lambda_{max}=872$, 719, 644, 599, 547, 484 nm; MALDI-MS: isotopic clusters at *m/z* (%): 3043.1 (2) [*M*−Pc]$^+$, 2933.2 (12) [*M*−CdPc]$^+$, 1523.1 (100) [*M*−CdPc$_2$]$^+$, 1411.2 (45) [*M*−Cd$_2$Pc$_2$]$^+$; elemental analysis calcd (%) for $C_{288}H_{432}N_{24}Cd_2$: C 77.64, H 9.77, N 7.54; found: C 77.34, H 9.75, N 7.31].

**Tris[1,4,8,11,15,18,22,25-octakis(decyl)phthalocyaninate]dicadmium (1c)**: The product was prepared as for **1a** (method 1) from **3c**. The crude product was dissolved in hot $CH_2Cl_2$. Upon cooling, compound **3c** crystallised and was removed by filtration. The blue mother liquor was concentrated and methanol was added. A dark blue powder crystallised (15%). M.p. 109 °C (decomp); IR (neat, ATR): $\tilde{\nu}=2915.73$, 2846.2, 1604.07, 1465.67, 1366.71, 1264.2, 1189.6, 1096.9 $\mathrm{cm^{-1}}$; UV/Vis (*n*-hexane): $\lambda_{max}=718$, 647, 599, 550, 483 nm; MALDI-MS: isotopic clusters at *m/z* (%): 3380.6 (5) [*M*−CdPc]$^+$, 1747.3 (100) [*M*−CdPc$_2$]$^+$, 1635.4 (32) [*M*−Cd$_2$Pc$_2$]$^+$; elemental analysis calcd (%) for $C_{336}H_{528}N_{24}Cd_2$: C 78.69, H 10.38, N 6.55; found: C 78.56, H 10.47, N 6.71].

### Synthesis of metal-free 1,4,8,11,15,18,22,25-octakis(oct-7-enyl)phthalocyanine (2d)

*2-(Oct-7-enyl)furan*: In a typical experiment, *n*BuLi (2.5 M solution in hexanes, 17.6 mL, 44 mmol) was added to a solution of furan (5 g, 73.5 mmol) in dry THF (20 mL) with stirring under $N_2$ at −78 °C. The solution was allowed to warm to RT and stirred for 4 h before being cooled to −78 °C. 8-Bromooct-1-ene (12 g, 63 mmol) in dry THF (5 mL) was added dropwise and the solution allowed to warm to RT and stirred overnight. The solution was poured into ice/water (100 mL), the organic phase was extracted with ethyl acetate (3×50 mL), dried ($MgSO_4$), and filtered; the solvents were then removed under reduced pressure to afford a pale orange oil that was used without further purification (12.9 g, 100%). $^1$H NMR (60 MHz, $CDCl_3$): $\delta=7.3$ (m, 1H), 6.3 (m, 1H), 5.5–6.2 (m, 2H), 4.8–5.2 (m, 2H), 2.6 (t, $J=8$ Hz, 2H), 1.2–2.3 ppm (m, 10H).

*2,5-Bis(oct-7-enyl)furan*: In a typical experiment, *n*BuLi (2.5 M solution in hexanes, 25 mL, 63 mmol) was added to a solution of 2-(oct-7-enyl)furan (12.9 g, 63 mmol) in dry THF (20 mL) with stirring under $N_2$ at −78 °C. The solution was allowed to warm to RT and stirred for 4 h before being cooled to −78 °C. 8-Bromooct-1-ene (13 g, 68 mmol) in dry THF (10 mL) was added dropwise and the solution allowed to warm to RT and stirred overnight. The solution was poured into ice/water (100 mL), the organic phase was extracted with ethyl acetate (3×50 mL), dried ($MgSO_4$), and filtered; the solvents were then removed under reduced pressure to afford a pale orange oil. The unreacted 2-(oct-7-enyl)furan was removed by distillation leaving the product, which was used without further purification (19.2 g, 100%). $^1$H NMR (60 MHz, $CDCl_3$): $\delta=5.5$–6.2 (m, 2H), 5.8 (s, 2H), 4.8–5.2 (m, 4H), 2.6 (t, $J=8$ Hz, 4H), 2.0 (m, 4H), 1.7 ppm (br s, 16H).

*3,6-Bis(oct-7-enyl)phthalonitrile*: In a typical experiment, 2,5-bis(oct-7-enyl)furan (19.2 g, 63 mmol) and fumaronitrile (7 g, 90 mmol) were dissolved in the minimum amount of dry THF. The flask was sealed under $N_2$ and placed in the fridge for a minimum of 14 days. The cold solution was added to dry THF (20 mL) at −78 °C under $N_2$. Lithium trimethylsilyl bisamide (1 M in THF, 90 mL, 90 mmol) was added. The solution turns dark brown and was allowed to warm to RT and stirred for 2 h. The solution was poured into ice/aq. $NH_4Cl$ (100 mL) and the organic phase was extracted with ethyl acetate (3×50 mL), dried ($MgSO_4$) and filtered; the solvents were then removed under reduced pressure. The brown residue was purified by column chromatography on silica (eluent: petroleum ether (bp. 40–60 °C)/ethyl acetate 10:1). A first fraction was collected which contained 2,5-bis(oct-7-enyl)furan (1.8 g). The second fraction contained the desired compound 3,6-bis(oct-7-enyl)phthalonitrile as a colourless oil (3.58 g, 16 %). M.p. 34.4 °C; $^1$H NMR (60 MHz, $CDCl_3$): $\delta = 7.4$ (s, 2 H), 5.4–6.0 (m, 2 H), 4.7–5.2 (m, 4 H), 2.8 (t, $J = 8$ Hz, 4 H), 1.2–2.2 ppm (m, 20 H); $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta = 146.25$, 138.97, 133.46, 115.76, 115.14, 114.39, 34.27, 33.54, 30.51, 28.86, 28.6, 28.58 ppm; IR (neat, ATR): $\tilde{\nu} = 2228.06$ (CN), 1638.15 cm$^{-1}$ (C=C); EI-MS: *m/z* (%): 348 (20) $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{32}N_2$: C 82.71, H 9.25, N 8.04; found: C 82.42, H 9.38, N 7.84].

*Metal-free 1,4,8,11,15,18,22,25-octakis(oct-7-enyl)phthalocyanine (**2d**)*: In a typical experiment 3,6-bis(oct-7-enyl)phthalonitrile (1.38 g, 4 mmol) in pentanol (10 mL) was brought to reflux. Lithium metal (excess) was added in portions to the refluxing solution and reflux was continued for 6 h. The solution was then left to cool and acetic acid (3 mL) was added. Stirring was continued for 30 min. Excess methanol was added and the mixture placed in the fridge overnight. The precipitate was collected by filtration and washed with methanol. The product was recrystallised from THF/methanol to afford dark green fine needles (520 mg, 38 %). M.p. K–D 80.7 °C, D–D 130.5 °C, D–I 151.7 °C; $^1$H NMR (270 MHz, $C_6D_6$): $\delta = 7.78$ (s, 8 H), 5.6–5.8 (m, 8 H), 4.9–5.1 (m, 16 H), 4.59 (t, $J = 7.6$ Hz, 16 H), 2.22 (m, 16 H), 1.93 (m, 16 H), 1.69 (m, 16 H), 1.3–1.5 (m, 32 H), −0.39 ppm (s, 2 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$): $\delta = 139.07$, 139.02, 131.11, 114.43, 33.95, 33.07, 30.94, 29.63, 29.57, 29.13 ppm. IR (neat, ATR): $\tilde{\nu} = 3292.42$ (NH), 1640.35 cm$^{-1}$ (C=C); UV/Vis (dichloromethane): $\lambda_{max}$ ($\varepsilon$) = 727 ($0.63 \times 10^5$), 700 nm ($0.52 \times 10^5$ mol$^{-1}$ dm$^3$ cm$^{-1}$); FAB MS: *m/z* (%): 1396.2 (30) $[M]^+$; elemental analysis calcd (%) for $C_{96}H_{130}N_8$: C 82.59, H 9.39, N 8.03; found: C 82.6, H 9.36, N 7.84.

**1,4,8,11,15,18,22,25-Octakis(oct-7-enyl)phthalocyaninatocadmium (3d)**: In a typical experiment, **2d** (100 mg, 72 µmol) in pentanol (5 mL) was brought to reflux. Cadmium acetate (4 equiv, excess) was added and reflux was continued for 45 min. The hot solution was poured into methanol (50 mL) and the flask placed in the fridge. The green precipitate was filtered then dissolved in THF (20 mL) through the filter paper, leaving the excess cadmium acetate. The green solution was concentrated and methanol (20 mL) was added. The flask was placed in the fridge. The green precipitate was filtered and washed with methanol to afford the product (85 mg, 78 %). M.p. K–D 70.7 °C, D–D 133.0 °C, D–I 209.4 °C; $^1$H NMR (400 MHz, [D$_8$]THF): $\delta = 7.8$ (s, 8 H), 5.66–5.75 (m, 8 H), 4.78–4.90 (m, 16 H), 4.57 (t, $J = 9.2$ Hz, 16 H), 2.19 (m, 16 H), 1.96–1.99 (m, 16 H), 1.64 (m, 16 H), 1.37 ppm (m, 32 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$ containing a drop of [D$_5$]pyridine): $\delta = 155.36$, 139.18, 138.58, 136.71, 130.29, 114.33, 33.96, 32.99, 31.32, 29.69, 29.47, 29.13 ppm; IR (neat, ATR): $\tilde{\nu} = 3073.88$, 2921.09, 2850.24, 1639.96 (C=C), 1316.11, 1082.11, 989.85, 906.25, 808.7 cm$^{-1}$; UV/Vis (THF): $\lambda_{max} = 707$ nm; UV/Vis (dichloromethane): $\lambda_{max} = 712$ nm; FAB MS: *m/z* (%): 1507.9 (100) $[M]^+$; elemental analysis calcd (%) for $C_{96}H_{128}N_8Cd$: C 76.54, H 8.56, N 7.44; found: C 76.15, H 8.34, N 7.25].

**Tris[1,4,8,11,15,18,22,25-octakis(oct-7-enyl)phthalocyanine]dicadmium (1d)**: In a typical experiment, compound **3d** (50 mg, 33 µmol) was recrystallised slowly from dichloromethane/methanol to afford the product as a dark blue/black powder (23 mg, 56 %). M.p. D–I 152.3 °C; IR (neat, ATR): $\tilde{\nu} = 2918.08$, 2847.58, 1603.81, 1365.58, 1274.01, 904.98 cm$^{-1}$; UV/Vis (*n*-hexane): $\lambda_{max} = 719$, 600, 483 nm; MALDI-MS: isotopic clusters at *m/z* (%): 3012.6 (3) $[M{-}Pc]^+$, 2899.7 (10) $[M{-}PcCd]^+$, 1506.8 (100) $[M{-}Pc_2Cd]^+$; elemental analysis calcd (%) for $C_{288}H_{384}N_{24}Cd_2$: C 78.49, H 8.78, N 7.63; found: C 78.49, H 8.87, N 7.56].

### Synthesis of metal-free 2,3,9,10,16,17,23,24-octakis(2-ethyl-1-hexyl)phthalocyanine (5a)

**4,5-Bis(2-ethylhexyl)phthalonitrile**: The product was obtained from 4,5-dichlorophthalonitrile (2 g, 0.01 mol) and 2-ethylhexyl zinc bromide (50 mL of 0.5 M solution in THF) following the method described for the synthesis of **5b** below. The compound was separated and purified by column chromatography, which afforded two products, 4-(2-ethylhexyl)phthalonitrile (0.3 g) and the desired product (1.2 g, 34 %). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.52$ (s, 2 H), 2.6 (d, $J = 7.2$ Hz, 4 H), 1.55 (quint, $J = 6.2$ Hz, 2 H), 1.16–1.33 (m, 16 H), 0.86–0.89 ppm (m, 12 H); $^{13}$C NMR (100.55 MHz, $CDCl_3$): $\delta = 147.08$, 134.85, 115.81, 112.42, 40.37, 37.05, 32.26, 28.6, 25.44, 22.86, 13.97, 10.69 ppm. IR (neat, ATR): $\tilde{\nu} =$ 2227.8 cm$^{-1}$ (CN); EI-MS: *m/z* 352.3 $[M]^+$; CI-MS: *m/z* 370.3 $[M{+}NH_3]^+$.

*Metal-free 2,3,9,10,16,17,23,24-octakis(2-ethyl-1-hexyl)phthalocyanine (**5a**)*: The product was prepared as for **2d** using 4,5-bis(2-ethylhexyl)-phthalonitrile (1.2 g, 3.4 mmol). This yielded metal-free **5a** (420 mg, 35 %). M.p. 280.3 °C; $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 9.69$ (s, 8 H), 3.17 (m, 16 H), 2.06 (m, 8 H), 1.33–1.63 (m, 64 H), 0.93–1.02 (m, 48 H), −0.24 ppm (s, 2 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$): $\delta = 143.18$, 135.7, 41.17, 38.6, 32.79, 28.98, 26.03, 23.16, 14.01, 10.94 ppm; IR (neat, ATR): $\tilde{\nu} =$ 2387.6 (NH), 2955.03, 2922.04, 2855.84, 1456.35, 1104.11, 1010.29, 894.98 cm$^{-1}$; UV/Vis (THF): $\lambda_{max} = 706$, 669 nm; MALDI MS: isotopic cluster at *m/z* (%) 1412.1 (100) $[M]^+$; elemental analysis calcd (%) for $C_{96}H_{146}N_8$: C 81.64, H 10.42, N 7.93; found: C 81.48, H 10.43, N 7.63].

### Synthesis of metal-free 2,3,9,10,16,17,23,24-octakis(hexyl)phthalocyanine (5b)

*4,5-Bis(hexyl)phthalonitrile*: In a typical experiment, triphenylphosphine (1.25 g, 5 mmol), $[NiCl_2(PPh_3)_2]$ (1.56 g, 2.5 mmol) and LiCl (3 g, 70 mmol) were stirred in dry THF (50 mL) under $N_2$ atmosphere to yield a blue solution. A solution of 2.5 M *n*BuLi in hexanes (2 mL, 5 mmol) was added through a syringe and the solution turned deep red. 4,5-Dichlorophthalonitrile[35] (5 g, 25 mmol) was added at once and the solution changed colour to light brown. This was left to stir for a few minutes, and then the solution was cooled down to −78 °C. A solution of hexylzincbromide in THF (0.5 M, 100 mL, 50 mmol) was added dropwise. The mixture was left to warm to room temperature and was stirred overnight. The solution was poured into 5 % aqueous HCl (100 mL) and the organic phase was extracted with ethyl acetate ($2 \times 50$ mL). It was further washed with 5 % aq. HCl (30 mL), 5 % aq. NaOH (30 mL) and brine (30 mL), dried ($MgSO_4$) and filtered; the solvents were then removed under reduced pressure. TLC analysis (eluent: petroleum ether (b.p. 40–60 °C)/dichloromethane 1:1) indicated three main products that were separated by column chromatography on silica. A first separation was performed (eluent: petroleum ether (b.p. 40–60 °C)/dichloromethane 1:1) and two fractions were obtained: the first containing triphenylphosphine, the second a mixture of products. A second separation was performed on this latter fraction (eluent: petroleum ether (b.p. 40–60 °C)/ethylacetate 5:1). Three products were obtained and identified by $^1$H NMR spectroscopy as 1) 4-hexylphthalonitrile: $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.7$ (d, $J = 10$ Hz, 1 H), 7.59 (s, 1 H), 7.52 (d, $J = 10$ Hz, 1 H), 2.7 (t, $J = 7.6$ Hz, 2 H), 1.6 (quint, $J = 7.2$ Hz, 2 H), 1.29 (m, 6 H), 0.81 ppm (t, $J = 7.6$ Hz, 3 H) ppm; 2) 4-chloro-5-hexylphthalonitrile: $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (s, 1 H), 7.68 (s, 1 H), 2.79 (t, $J = 7.6$ Hz, 2 H), 1.62 (quint, $J = 7.6$ Hz, 2 H), 1.22–1.38 (m, 6 H), 0.88 ppm (t, $J = 7.2$ Hz, 3 H); and 3) the desired 4,5-bis(hexyl)phthalonitrile (1.12 g, 15 %): $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.57$ (s, 2 H), 2.67 (t, $J = 7.6$ Hz, 4 H), 1.55 (quint, $J = 7.6$ Hz, 4 H), 1.23–1.4 (m, 12 H), 0.85 ppm (t, $J = 7.2$ Hz, 6 H).[36]

*Metal-free 2,3,9,10,16,17,23,24-octakis(hexyl)phthalocyanine (**5b**)*: The product was prepared as for **2d** using 4,5-bis(hexyl)phthalonitrile (1.12 g, 3.75 mmol). This yielded metal-free **5b** (500 mg, 45 %). M.p. K–D 250.4 °C, D-I >300 °C (decomp); IR (neat, ATR): $\tilde{\nu} = 3290.21$ (NH), 2918.72, 2850.86, 1463.39, 1321.15, 1102.91, 1009.48, 752.24, 705.63 cm$^{-1}$; UV/Vis (THF): $\lambda_{max} = 704.5$, 666.5 nm; MALDI-MS: isotopic cluster at *m/z* (%) 1186.9 (100) $[M]^+$; elemental analysis calcd (%) for $C_{80}H_{114}N_8$: C 80.89, H 9.67, N 9.43; found: C 80.46, H 9.48, N 9.43.

**2,3,9,10,16,17,23,24-Octakis(2-ethyl-1-hexyl)phthalocyaninatocadmium (6a)**: The product was prepared as for **3a** from **5a** (100 mg, 71 µmol). This yielded **6a** as a green powder (100 mg, 94 %). M.p. 248.7 °C; $^1$H NMR(400 MHz, [D$_8$]THF): $\delta = 9.14$ (s, 8 H), 3.18 (m, 16 H), 2.04 (m, 8 H), 1.28–1.75 (m, 64 H), 1.05 (t, $J = 7.2$ Hz, 24 H), 0.95 ppm (t, $J = 7.2$ Hz, 24 H); $^{13}$C NMR (75.4 MHz, $C_6D_6$ + a drop of [D$_5$]pyridine): $\delta =$ 155.93, 141.95, 138.03, 124.71, 41.41, 38.73, 32.99, 29.18, 26.15, 23.35, 14.21, 11.12 ppm; IR (neat, ATR): $\tilde{\nu} = 2954.64$, 2920.0, 2855.09, 1454.29, 1305.94, 1080.48, 751.84, 720.67 cm$^{-1}$; UV/Vis (THF): $\lambda_{max} = 688$, 621 nm; UV/Vis ($CH_2Cl_2$): $\lambda_{max} = 697$, 605 nm; MALDI-MS: isotopic clusters at *m/z* (%): 1523.0 (100) $[M]^+$, 2932.1 (10) $[Pc_2Cd]^+$, 3044.9 (60) $[Pc_2Cd_2]^+$; elemental analysis calcd (%) for $C_{96}H_{144}N_8Cd{\cdot}2\,CH_3OH$: C 74.23, H 9.66, N 7.07; found: C 74.25, H 9.67, N 6.67].

**2,3,9,10,16,17,23,24-Octakis(hexyl)phthalocyaninatocadmium (6b)**: The product was prepared as for **3a** from **5b** (30 mg, 25 μmol). The hot solution was poured into excess acetone and the product filtered. This yielded **6b** as a blue powder (22 mg, 67 %). M.p. >300 °C; $^1$H NMR (400 MHz, $C_6D_6$ + a drop of [$D_5$]pyridine): $\delta$ = 9.67 (s, 8H), 3.08 (t, $J$ = 7.6 Hz, 16H), 1.87 (quint, $J$ = 7.6 Hz, 16H), 1.48 (m, 16H), 1.3 (m, 32H), 0.91 ppm (t, $J$ = 7.2 Hz, 24H); $^{13}$C NMR (75.4 MHz, $C_6D_6$ + a drop of [$D_5$]pyridine): $\delta$ = 155.92, 142.45, 139.29, 126.84, 34.09, 32.08, 31.96, 29.89, 22.82, 14.11 ppm; IR (neat, ATR): $\tilde{\nu}$ = 2955.67, 2921.58, 2855.14, 1555.77, 1403.3, 1095.36, 1021.38, 748.67, 665.96 cm$^{-1}$; UV/Vis (THF): $\lambda_{max}$ = 686, 619 nm; MALDI-MS: isotopic clusters at *m/z* (%): 1298.8 (30) [$M$]$^+$, 1186.9 (10) [$M$−Cd]$^+$; elemental analysis calcd (%) for $C_{80}H_{112}N_8Cd{\cdot}2\,MeOH$: C 72.29, H 8.87, N 8.22; found: C 72.33, H 8.46, N 7.8.

**Tris[2,3,9,10,16,17,23,24-octakis(2-ethyl-1-hexyl)phthalocyaninate]dicadmium (7a)**: The product was prepared as for **1a** from **6a** (50 mg, 36 μmol). This yielded **7a** as a dark powder (53 mg, 73 %). M.p. 274 °C; IR (neat, ATR): $\tilde{\nu}$ = 2920.0, 1454.23, 1304.0, 1103.65, 747.76, 718.36 cm$^{-1}$; UV/Vis (hexane): $\lambda_{max}$ = 693, 615, 495, 334 nm; MALDI-MS: isotopic clusters at *m/z* (%): 4455.2 (100) [$M$]$^+$, 3045.1 (65) [$M$−Pc]$^+$, 2933.3 (10) [$M$−PcCd]$^+$, 1523.1 (60) [$M$−$Pc_2Cd$]$^+$; elemental analysis calcd (%) for $C_{288}H_{432}N_{24}Cd_2$: C 77.64, H 9.77, N 7.54; found: C 77.59, H 9.67, N 7.56.

**Recrystallisation of 6b**: Complex **6b** (22 mg, 17 μmol) was recrystallised from dichloromethane and methanol to afford a dark blue powder (12 mg). M.p. >300 °C; IR (neat, ATR): $\tilde{\nu}$ = 2915.23, 2848.07, 1499.16, 1456.65, 1361.95, 1314.5, 1103.25, 749.88, 718.34 cm$^{-1}$; UV/Vis (hexane): $\lambda_{max}$ = 678, 642, 480, 329 nm; MALDI-MS: isotopic clusters at *m/z* (%): 7676.7 (20), 6377.0 (70), 5081.3 (100), 3895.4 (25), 2596.9 (20), 1296.9 (15).

**Synthesis of 2(3),9(10),16(17),23(24)-tetra-*tert*-butylphthalocyaninato cadmium (8)**: 2(3),9(10),16(17),23(24)-Tetra-*tert*-butylphthalocyanine (120 mg, 0.16 mmol) in pentanol (10 mL) was brought to reflux. Cadmium acetate (4 equiv, excess) was added and reflux continued for 45 min. The hot solution was poured into methanol (50 mL) and the flask placed in the fridge. The insoluble blue precipitate was filtered and washed with methanol to afford the product (45 mg, 33 %). UV/Vis (dichloromethane): $\lambda_{max}$ = 683, 660, 635 nm.

**Synthesis of 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)porphyrinato cadmium (9)**: 5,10,15,20-Tetra(3,5-di-*tert*-butylphenyl)porphyrin (100 mg, 94 μmol) in pentanol (10 mL) was brought to reflux. Cadmium acetate (4 equiv, excess) was added and reflux continued for 45 min. The hot solution was poured into methanol (50 mL) and the flask placed in the fridge. The purple precipitate was filtered and washed with methanol to afford the product (73 mg, 66 %). UV/Vis (dichloromethane): $\lambda_{max}$ = 432, 564, 604 nm; MALDI-MS: isotopic clusters at *m/z* (%): 1174.7 (100) [$M$]$^+$, 1063.8 (10) [$M$−Cd]$^+$.

**Experiment 1**: Compounds **3a** (20.4 mg, 15.7 μmol) and **2d** (10.9 mg, 7.84 μmol) were dissolved in $CH_2Cl_2$ (2 mL). Two drops of methanol were added and the solution cooled to 4 °C. After 24 h excess methanol was added and the product left to precipitate overnight. This was filtered to afford a dark blue powder (21 mg). $^1$H NMR (400 MHz, $CDCl_3$) (selected data): $\delta$ = 6.04–6.15 (m, $H$−C(R)=$CH_2$), 5.6–5.72 (m, $H$−C(R)=$CH_2$), 5.14–5.3 (m, H−C(R)=C$H_2$), 4.78–4.9 ppm (m, H-C(R)=C$H_2$); MALDI-MS: isotopic clusters at *m/z* (%): 1298.8 (100), 1506.9 (40), 2483.6 (60), 2691.7 (25), 2898.9 (5).

**Experiment 2**: This was achieved following the conditions described in Experiment 1 with **3a** (26.9 mg, 20.8 μmol) and **5a** (14 mg, 10 μmol). A dark blue powder was obtained (16 mg). MALDI-MS: isotopic clusters at *m/z* (%): 1186.9 (100), 1298.8 (35), 1522.1 (7), 2484.8 (6), 2709 (30), 4005.9 (10), 4232.3 (3), 4456.5 (5), 5528.2 (4).

**Experiment 3**: This was achieved following the conditions described in Experiment 1 with **1a** (20.6 mg, 5.5 μmol) and **5a** (4 mg, 2.8 μmol). A dark blue powder was obtained (18 mg). MALDI-MS: isotopic clusters at *m/z* (%): 1186.8 (100), 1298.7 (10), 1412 (18), 1522.9 (6), 2708.7 (20), 2931.9 (3), 4006.4 (5), 4229.7 (3), 4453.9 (5), 5528.6 (3), 5750.8 (2).

**Experiment 4**: This was achieved following the conditions described in Experiment 1 with **1a** (15.4 mg, 4.1 μmol) and **6a** (3.4 mg, 2.2 μmol). A dark blue powder was obtained (15 mg). MALDI-MS: isotopic clusters at *m/z* (%): 1186.8 (60), 1298.7 (100), 2484.5 (47), 2708.8 (5), 4007.6 (7), 4455 (1).

**Experiment 5**: This was achieved following the conditions described in Experiment 1 with **7a** (17.8 mg, 4 μmol) and **2a** (2.7 mg, 2.2 μmol). A dark blue powder was obtained (12 mg). MALDI-MS: isotopic clusters at *m/z* (%): 1186.8 (73), 1523 (25), 2710.8 (5), 2933.1 (7), 3044.9 (22), 4455 (100), 5526.5 (2).

**Experiment 6**: This was achieved following the conditions described in Experiment 1 with **7a** (16 mg, 3.6 μmol) and **3a** (2 mg, 1.6 μmol). A dark blue powder was obtained (14 mg). MALDI-MS: isotopic clusters at *m/z* (%): 1298.7 (19), 1411.1 (32), 1523 (37), 2707.9 (20), 2933.1 (30), 4455.1 (100).

## Acknowledgements

We thank the EPSRC and the Iceni Seedcorn Fund LLP for financial support and the former for access to the MS Service at Swansea (UK). We also thank Dr. A. N. Cammidge and Dr. M. R. Cheesman for invaluable discussions and advice during the course of the program.

---

[1] a) N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, (Eds.: B. Dunn, J. W. Goodby, A. R. West), Cambridge University Press, Cambridge (UK), **1998**; b) *The Porphyrin Handbook, Vols. 15–19*, (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press (USA), **2003**; c) *Phthalocyanines: Properties and Applications, Vols. 1–4*, (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, Weinheim (Germany), **1996**.

[2] P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum, New York, **1991**.

[3] P. Gregory, *J. Porphyrins Phthalocyanines* **2000**, *4*, 432–437.

[4] T. Shima, Y. Yamakawa, T. Nakano, J. Kim, J. Tominaga, *Jpn. J. Appl. Phys. Part 2* **2006**, *45*, L1007–L1009.

[5] H. Mustroph, M. Stollenwerk, V. Bressau, *Angew. Chem.* **2006**, *118*, 2068–2087; *Angew. Chem. Int. Ed.* **2006**, *45*, 2016–2035.

[6] Y. Sato, K. Yamagishi, M. Yamashita, *Opt. Rev.* **2005**, *12*, 324–327.

[7] R. Zhou, F. Josse, W. Gopel, Z. Z. Ozturk, O. Bekaroglu, *Appl. Organomet. Chem.* **1996**, *10*, 557–577.

[8] a) S. R. Flom in *The Porphyrin Handbook, Vol. 19* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, Boston, **2003**, pp. 179–189; b) G. de la Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *Chem. Rev.* **2004**, *104*, 3723–3750.

[9] D. Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, A. Slodek, *J. Porphyrins Phthalocyanines* **2004**, *8*, 1020–1041.

[10] a) E. A. Luk'yanets, *J. Porphyrins Phthalocyanines* **1999**, *3*, 424–432; b) H. Ali, J. E. van Lier, *Chem. Rev.* **1999**, *99*, 2379–2450.

[11] R. Weiss, J. Fischer in *The Porphyrin Handbook, Vol. 16* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, Elsevier Science (USA), **2003**, pp. 171–246.

[12] J. Janczak, R. J. Kubiak, *J. Chem. Soc. Dalton Trans.* **1993**, 3809–3812.

[13] J. Janczak, R. J. Kubiak, J. Richter, H. Fuess, *Polyhedron* **1999**, *18*, 2775–2780.

[14] J. A. de Saja, M. L. Rodriguez-Mendez, *Adv. Colloid Interface Sci.* **2005**, *116*, 1–11.

[15] H. Homborg, W. Kalz, *Z. Naturforsch. B* **1978**, *33*, 968–975.

[16] H. Homborg, C. L. Teske, *Z. Anorg. Allg. Chem.* **1985**, *527*, 45–61.

[17] a) H. Sugimoto, T. Higashi, M. Mori, *J. Chem. Soc. Chem. Commun.* **1983**, 622–623; b) H. Sugimoto, M. Mori, H. Masuda, T. Taga, *J. Chem. Soc. Chem. Commun.* **1986**, 962–963; c) V. B. Zhukhovitskii, N. N. Ezhova, V. I. Krinichnyi, Y. A. Letuchii, A. M. Tonshin, K. M. Dyumaev, M. L. Khidekel, *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1985**, *34*, 2493–2497.

[18] P. Turek, P. Petit, J. J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaud, M. Maitrot, *Mol. Cryst. Liq. Cryst.* **1988**, *161*, 323–327.
[19] L. G. Tomilova, E. V. Chernykh, N. T. Ioffe, E. A. Luk'yanets, *Zh. Obshch. Khim.* **1983**, *53*, 2594–2601.
[20] H. Sugimoto, T. Higashi, M. Mori, *Chem. Lett.* **1983**, 1167–1170.
[21] C. Clarisse, M. T. Riou, *Inorg. Chim. Acta* **1987**, *130*, 139–144.
[22] N. Kobayashi, *Coord. Chem. Rev.* **2002**, *227*, 129–152.
[23] J. Janczak, R. Kubiak, A. Jezierski, *Inorg. Chem.* **1995**, *34*, 3505–3508.
[24] M. T. Riou, M. Auregan, C. Clarisse, *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *187*, 349–354.
[25] I. Chambrier, D. L. Hughes, J. C. Swarts, B. Isare, M. J. Cook, *Chem. Commun.* **2006**, 3504–3506.
[26] W. Chidawanyika, A. Ogunsipe, T. Nyokong, *New J. Chem.* **2007**, *31*, 377–384.
[27] R. D. George, A. W. Snow, P. F. McMillan, V. A. Burrows, *J. Am. Chem. Soc.* **1992**, *114*, 8286–8287.
[28] I. Chambrier, M. J. Cook, M. Helliwell, A. K. Powell, *J. Chem. Soc. Chem. Commun.* **1992**, 444–446.
[29] N. Kobayashi, H. Ogata, N. Nonaka, E. A. Luk'yanets, *Chem. Eur. J.* **2003**, *9*, 5123–5134.
[30] M. J. Cook, I. Chambrier, B. Isare, WO 2005/105820, **2005**.
[31] N. B. McKeown, I. Chambrier, M. J. Cook, *J. Chem. Soc. Perkin Trans. 1* **1990**, 1169–1177.
[32] M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson, K. J. Harrison, *J. Chem. Soc. Perkin Trans. 1* **1988**, 2453–2458.
[33] A. N. Cammidge, M. J. Cook, K. J. Harrison, N. B. McKeown, *J. Chem. Soc. Perkin Trans. 1* **1991**, 3053–3058.
[34] T. K. Miyamoto, N. Sugita, Y. Matsumoto, Y. Sasaki, M. Konno, *Chem. Lett.* **1983**, 1695–1698.
[35] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, *Synthesis* **1993**, 194–196.
[36] M. Hanack, P. Haisch, H. Lehmann, L. R. Subramanian, *Synthesis* **1993**, 387–390.

Received: May 16, 2007