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Porphyrins with exocyclic rings. Part 24. Synthesis and spectroscopic properties of pyrenoporphyrins, potential building blocks for porphyrin molecular wires☆

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ABSTRACT

Porphyrins with fused pyrene units have been prepared by '2+2' and '3+1' methodologies. Nitration of 1,2,3,6,7,8-tetrahydropyrene, followed by oxidation with DDQ, gave 4-nitropyrene and this condensed with ethyl isocyanoacetate in the presence of DBU or a phosphazene base to generate a pyrenopyrrole ethyl ester. Ester saponification and decarboxylation with KOH in ethylene glycol at 190 °C gave the parent pyreno[4,5-*c*]pyrrole and this was further condensed with 2 equiv of acetoxymethylpyrroles to afford the corresponding tripyrranes protected at the terminal positions with *tert*-butyl esters. In a one pot procedure, the ester protective groups were cleaved with TFA and following dilution with dichloromethane, '3+1' condensation with a pyrrole dialdehyde, and dehydrogenation with DDQ, the targeted pyrenoporphyrins were generated in good overall yields. A dialdehyde was also prepared from the pyrenopyrrole intermediate and this reacted to give an *opp*-dipyrenoporphyrin. The pyrenopyrrole ethyl ester reacted with dimethoxymethane in the presence of an acid catalyst to give a dipyrenopyrrolylmethane, and this was used to prepare an *adj*-dipyrenoporphyrin using the MacDonald '2+2' approach. The pyrenopyrrole dialdehyde was also used to prepare a porphyrin with fused pyrene and phenanthroline moieties. Although the UV–vis spectra of these new porphyrin systems are unexceptional, pyrenoporphyrins show many of the features necessary for the construction of porphyrin molecular wires.

1. Introduction

Porphyrins have many properties that are desirable in supramolecular assemblies and nanomolecular architectures.[1] They are robust near planar systems that readily form metallo-derivatives, and metalloporphyrins may also have useful catalytic properties.[2] Axial coordination to a metalloporphyrin can produce assemblies with unique structural properties.[3] In addition, linkages from the *meso*-positions, or less commonly the β-positions, can be used to generate cavities with geometries that can help to direct specific chemical reactions.[4,5] Linked porphyrin systems have been designed as molecular wires,[6] and other assemblies are being investigated for molecular scale information storage devices.[7] Molecular wires do not require the presence of continuously conjugated π-system, but conjugated oligoporphyrin systems have been widely investigated with this goal in mind.[8,9] Crossley and co-workers have synthesized oligoporphyrin 'wires', such as **1** and **2** by reacting *meso*-tetraaryl chlorin dione **3** and bacteriochlorin tetraone **4** with 1,2,4,5-benzenetetraamine (Chart 1).[8,9] A related anthroquinone linked porphyrin dimer **5** has also been reported, although a very different synthetic approach was used in this case.[10] In other studies, Smith and coworkers have synthesized a fused porphyrin 'trimer' **6** using the pyrroloporphyrin derived from 2-nitroTPP **7** (Scheme 1).[11] An alternative strategy enabled the same group to prepare the cruciform porphyrin pentamer **8** (Chart 1).[12] More recently, extended *meso*-*meso*,β-β,β-β-triply fused molecular tapes have been prepared by the oxidation of *meso*-*meso*-linked porphyrin oligomers,[13] and this strategy has been adapted to the synthesis of a tetrameric porphyrin sheet with a cyclooctatetraene core.[14]

As supramolecular assemblies of this type are attracting increasing attention, alternative strategies for synthesizing conjugated porphyrinoid arrays are still of great interest. The geometry of the porphyrin nucleus allows structural moieties fused to the individual pyrrole units to be orientated in a linear fashion, or at right angles, essentially providing the connectivity of a molecular mechano or lego set. Although directly fused porphyrins can be generated,[11] connecting units, such as the quinoxaline-type bridges investigated by Crossley and Burn allow for greater control over the properties of the resulting oligomers.[8,9] In our studies, we

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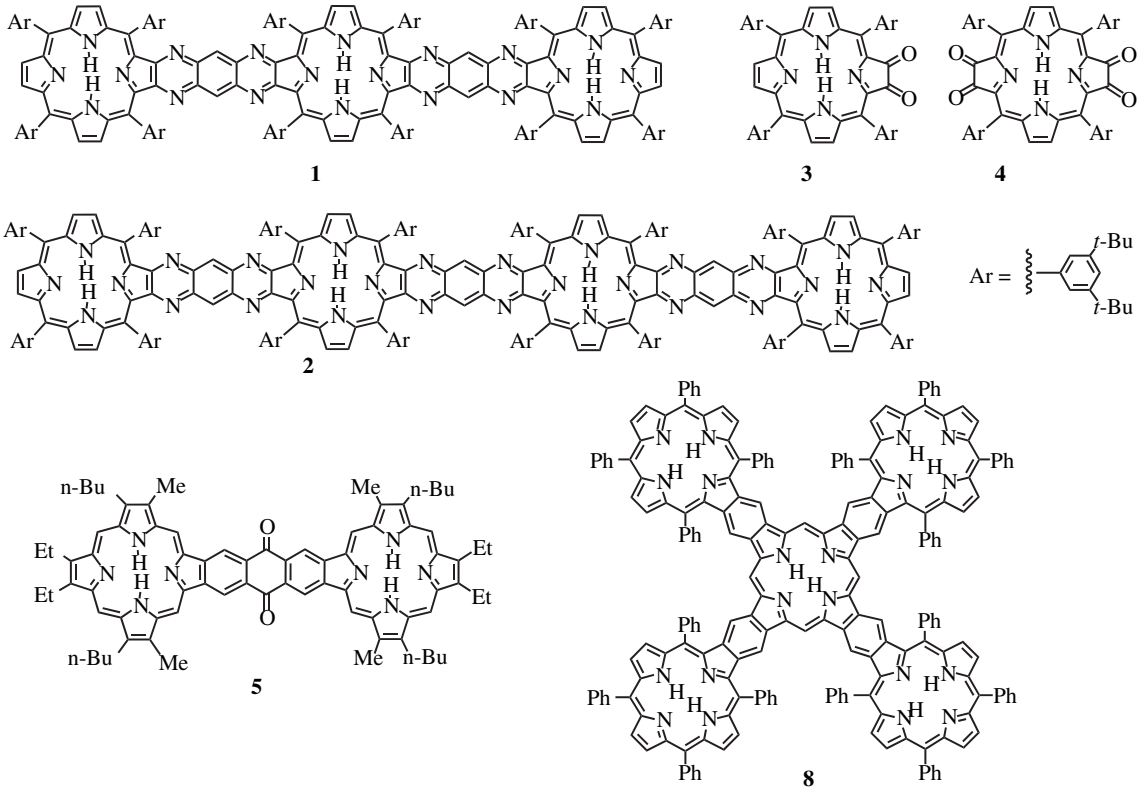
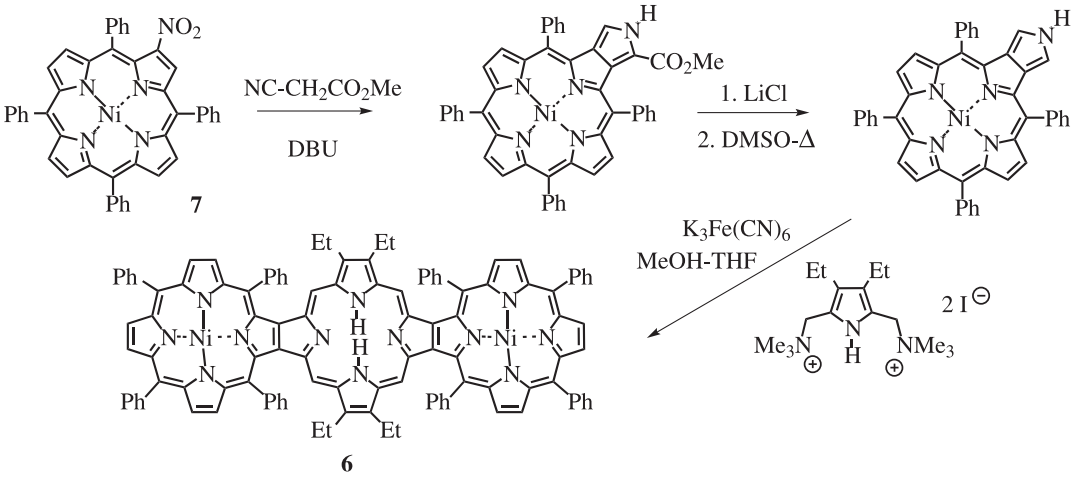
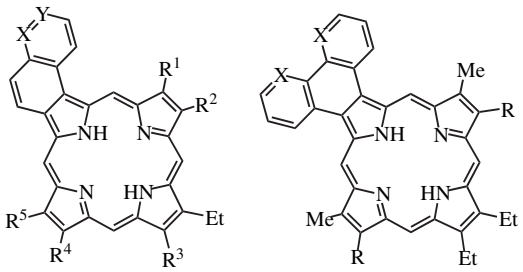


Chart 1.



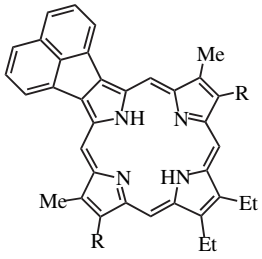
Scheme 1.

have developed syntheses of porphyrins with fused aromatic units, such as naphthalene (**9**),[15] quinoline (**10a**),[16] isoquinoline (**10b**),[16] phenanthrene (**11a**),[17] phenanthroline (**11b**),[18] acenaphthylene (**12**),[19,20] fluoranthene,[21] and benzothiadiazole (**13a**)[19,22] (Chart 2). These porphyrins were synthesized by first constructing pyrrole precursors with the required fused aromatic subunits,[23] and then taking these on using the MacDonald '2+2' or '3+1' strategies.[24] In most of these syntheses, the pyrroles were prepared using a Barton–Zard-type synthesis[25,26] by reacting isocyanoacetates with nitroaromatic compounds in the presence of a non-nucleophilic base such as DBU.[23,27] In order for this chemistry to occur, the nitroaromatic compound must have sufficient nitroalkene character to undergo an initial Michael-type addition, and in some cases better results are achieved using a phosphazene base.[28,29] In principle, this strategy could be used to prepare conjugated porphyrin dimers and oligomers. In particular, pyrene linked porphyrin chains **14** might be obtained from suitably substituted pyrrolic precursors. Pyrene provides 'flat edges' that are parallel to one another and this allows the desired geometry of the porphyrin nucleus to be extended outwards while leaving positions open for the introduction of substituents that may be needed for solubility or to fine tune the electronic properties of the oligoporphyrin chain. In order to explore the feasibility of this strategy, a synthesis of pyrenoporphyrins **15** has been developed. It was anticipated that this annelated porphyrin could be constructed using the pyrenopyrrole precursor **16** (Scheme 2), and this might in turn be accessible by reacting ethyl isocyanoacetate with 4-nitropyrene (**17**).[30]

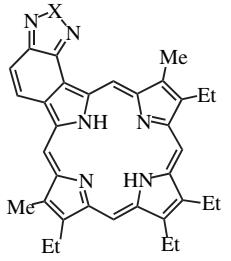


9 X = Y = CH;
$R^1 = R^3 = R^4 = Me$; $R^2 = R^5 = Et$
10 $R^2 = R^4 = Me$; $R^1 = R^3 = R^5 = Et$
a. X = N; Y = CH b. X = CH; Y = N

11a X = CH
11b X = N
R = Et or Bu

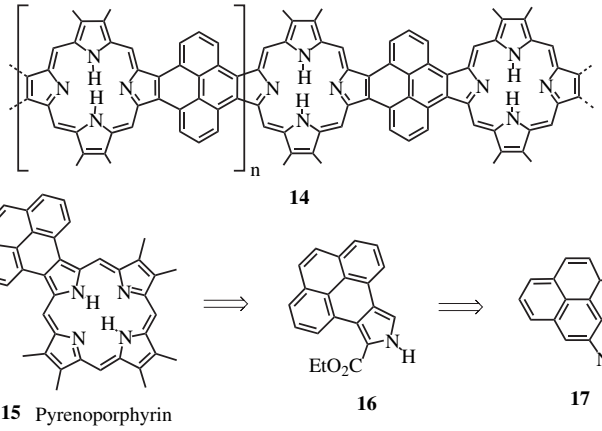


12
R = Et or $CH_2CH_2CO_2Me$



13 a. X = S;
b. X = O; c. X = Se

Chart 2.



14

15 Pyrenoporphyrin

16

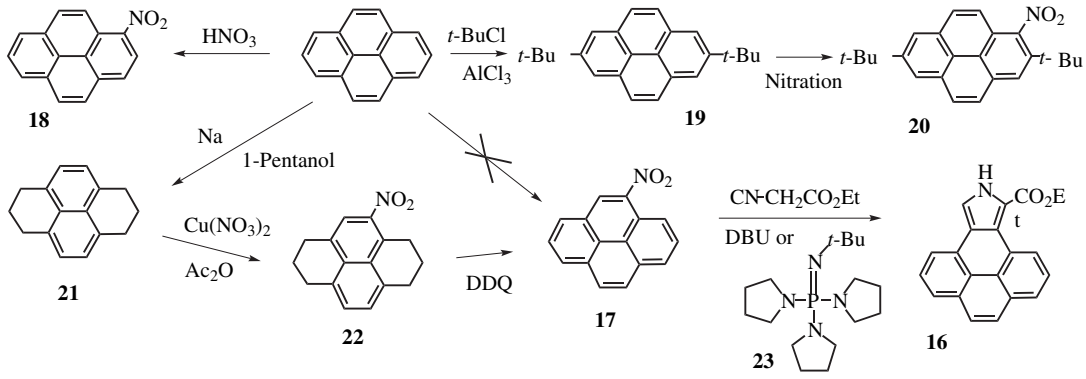
17

Scheme 2.

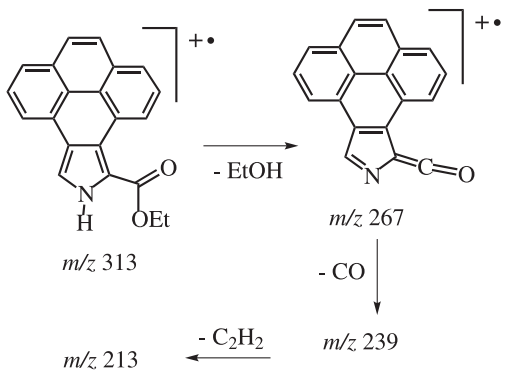
2. Results and discussion

2.1. Synthesis of pyrenoporphyrins and related systems

As nitroarenes are commonly used to prepare *c*-annelated pyrroles using the Barton–Zard reaction,[26,31] this method was explored for the synthesis of the required pyrenopyrrole precursors to pyrenoporphyrins. However, attempts to generate pyrrolic products by reacting commercially available 1-nitropyrene (**18**) with ethyl isocyanoacetate have so far been unsuccessful (Scheme 3). In any case, 4-nitropyrene is structurally far more compatible with the requirements for oligoporphyrin synthesis. Unfortunately, electrophilic substitution of pyrene strongly favors substitution at the 1-position,[32] although Friedel–Craft alkylation with *tert*-butyl chloride and $AlCl_3$ affords the 2,7-dialkylated product **19** due to the steric bulk of the *tert*-butyl moieties (Scheme 3).[33] It might be anticipated that nitration of di-*tert*-butylpyrene **19** would be diverted due to these same considerations but this is not the case as this reaction produces only the 1-nitropyrene product **20**.[34,35] 4-Nitropyrene (**17**) would be expected to have a much better chance of undergoing nucleophilic attack and therefore should react with ethyl isocyanoacetate and DBU to afford the related pyrrole. Although the required 4-nitropyrene cannot be synthesized directly, this substitution can be achieved in an indirect fashion.[36] Reduction of pyrene with sodium in refluxing 1-pentanol affords the hexahydropyrene **21**.[36,37] This compound can only react at the exposed β-positions of the remaining naphthalene unit and nitration with copper(II) nitrate in acetic anhydride yields the related nitro compound **22** in excellent yields.[36] Dehydrogenation with DDQ affords the required nitropyrene **17** and this further undergoes the Barton–Zard condensation with ethyl isocyanoacetate in the presence of DBU to give the pyrenopyrrole **16** (Scheme 3) in 40–50% yield. The yield was raised to 85–91% when the phosphazene base **23** was used in place of DBU. The proton NMR spectrum of **16** in $CDCl_3$ shows the NH resonance near 10.0 ppm and three 1H doublets for the pyrene moiety at 8.11, 8.30, and 10.06 ppm; the latter resonance is deshielded by the ester carbonyl unit. The remaining aromatic protons show up between 7.8 and 8.0 ppm, including the pyrrole CH, which is obscured by the pyrene resonances. As expected, in DMSO-d_6 the NH peak is shifted downfield to 12.9 ppm due to hydrogen bonding with the solvent, but the pyrrole CH resonance is also shifted downfield and resolves as a doublet at 8.4 ppm with a typical pyrrolic coupling constant J=3.2 Hz. The EI-MS for **16** shows the molecular ion at m/z 313 and a base peak at 267 corresponding to loss of EtOH (Scheme 4). Further loss of CO gives a fragment ion with m/z 239, and subsequent elimination of acetylene affords a peak at m/z 213.

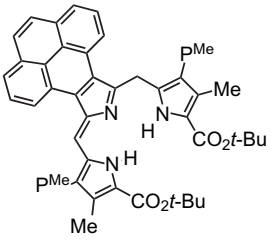


Scheme 3.

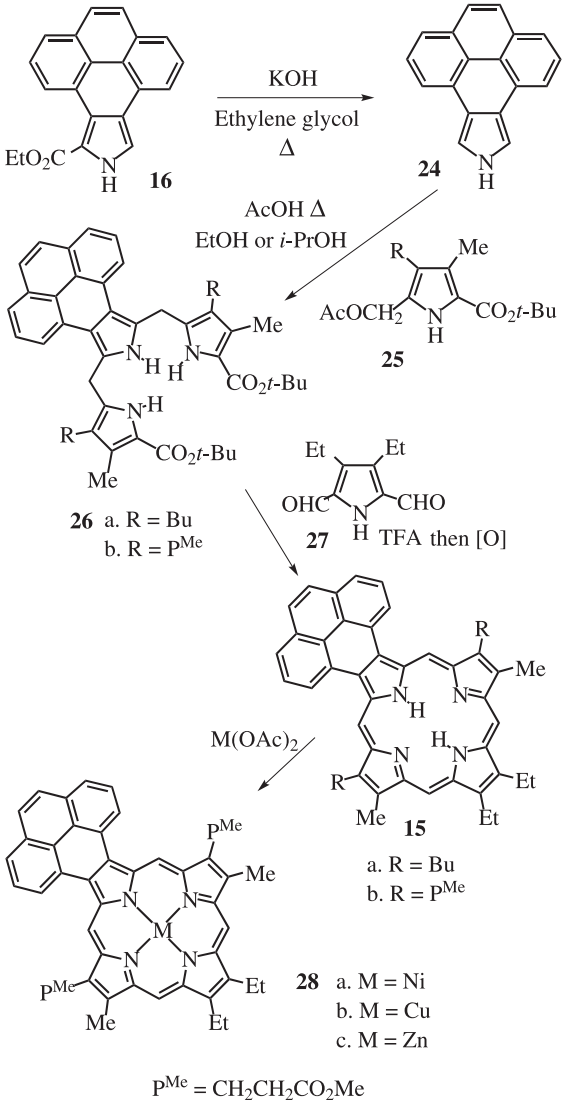


Scheme 4.

The availability of the pyrenopyrrole **16** not only allows the synthesis of monopyrenoporphyrins, but also makes related further annelated structures accessible such as *opp*-di- and *adj*-dipyrenoporphyrins. In most of these syntheses, tripyrrane intermediates were required and these could be prepared from the related pyrenopyrrole **24**. In order to prepare this intermediate, pyrrole **16** was saponified and decarboxylated with KOH in refluxing ethylene glycol and the unsubstituted pentacycle **24** was isolated in quantitative yield (Scheme 5). Further reaction with 2 equiv of acetoxymethylpyrroles **25** in refluxing ethanol or 2-propanol containing acetic acid as a catalyst gave the related tripyrranes **26**. On cooling, the *n*-butyl-substituted tripyrrane **26a** precipitated as a pure pink colored powder in 61% yield. However, the propionate ester version **26b** had to be precipitated out by adding the reaction solution to ice-water. The resulting tripyrrane was isolated in reasonably pure form in 72% yield. However, attempts to further purify **26b** by chromatography or recrystallization were unsuccessful. When **26b** was run through a silica column, an orange colored fraction corresponding to tripyrrene **26c** was isolated. Surprisingly, the tripyrrene was quite stable and could easily be purified and fully characterized.



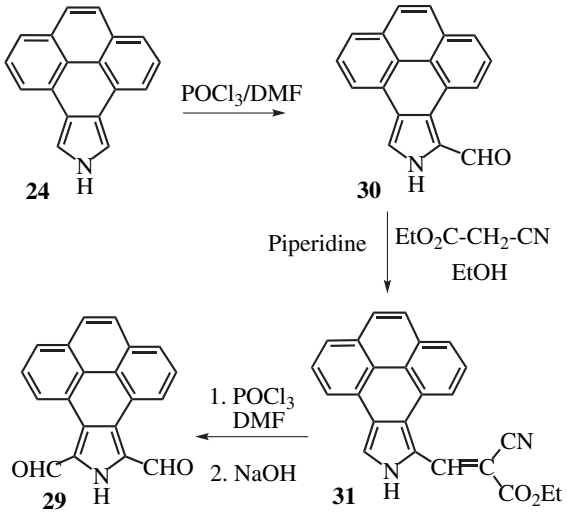
26c P^{Me} = $CH_2CH_2CO_2Me$
Tripyrrene by-product



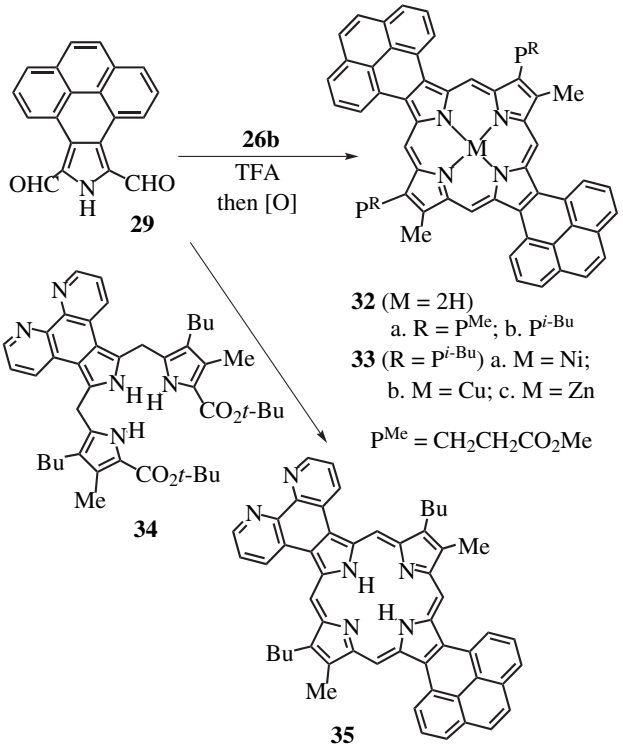
Scheme 5.

Cleavage of the *tert*-butyl ester moieties from **26a** with TFA, followed by condensation with diformylpyrrole **27** and oxidation with DDQ, gave the related pyrenoporphyrin **15a** in 40% yield (Scheme 5). The crude dipropionate ester tripyrrane **26b** was similarly reacted with TFA and **27**, although oxidation of the initial macrocyclic product was carried out with aqueous ferric chloride in this case,[38] and pyrenoporphyrin **15b** was isolated in 28% yield following chromatography and recrystallization from chloroform–methanol. Reaction of **15b** with nickel(II) acetate, copper(II) acetate or zinc acetate in chloroform–methanol or DMF gave the related metalloporphyrins **28a–c**.

The synthesis of an *opp*-dipyrenoporphyrin required the availability of a pyrenopyrrole dialdehyde **29**. This was prepared in three steps from unsubstituted pyrenopyrrole **24** (Scheme 6). Vilsmeier–Haack formylation of **24** afforded the monoaldehyde **30** and this was protected as the cyanovinyl derivative **31** by a Knoevenagel reaction with ethyl cyanoacetate in the presence of piperidine in refluxing ethanol. The protected pyrrole was further reacted with $POCl_3$–DMF to introduce a second formyl unit and subsequent cleavage of the cyanovinyl group with refluxing aqueous sodium hydroxide afforded the required dialdehyde **29**. The final step in this sequence can lead to poor yields for some pyrroles, but good overall yields were obtained in this case and the final step afforded **29** in quantitative yield. This was attributed to the poor solubility of the final product, which was forced out of the solution and was therefore not accessible for degradative side reactions to occur. The dialdehyde was reacted with tripyrrane **26b** under the '3+1' conditions, followed by oxidation with ferric chloride, to give *opp*-dipyrenoporphyrin **32a** (Scheme 7). However, this product proved to be highly insoluble and could not be properly characterized. For this reason, the diester was transesterified with sulfuric acid and isobutyl alcohol to give the diisobutyl ester **32b**. The straightforward extension of the side chains using a Fischer-type transesterification gave a dipyrenoporphyrin in 44% yield that was reasonably soluble and could be characterized by spectroscopic techniques such as UV–vis, proton NMR and carbon-13 NMR spectroscopy. Small samples of the related nickel(II), copper(II), and zinc complexes **33** were also prepared so that spectroscopic comparisons to the analogous monopyrenoporphyrins could be made.



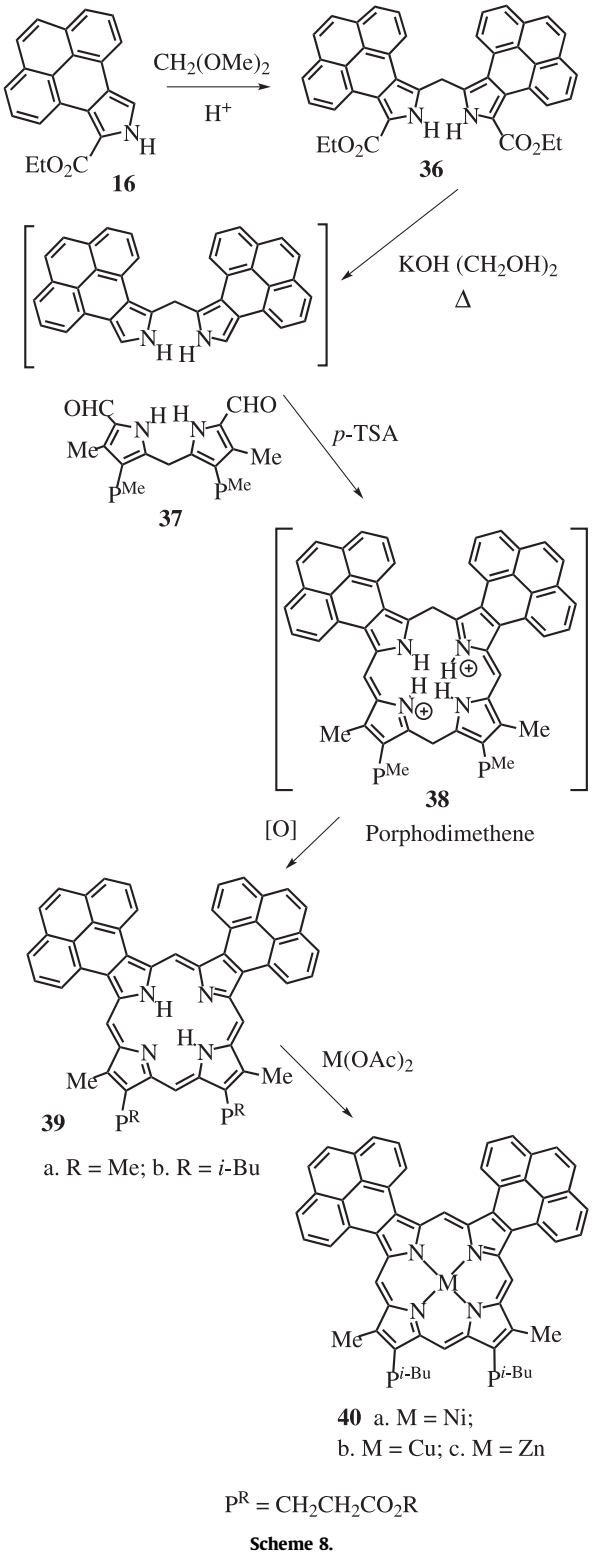
Scheme 6.



Scheme 7.

If these studies do lead to the construction of porphyrin molecular wires, a structural unit, that is, capable of acting as a connector to a cluster or a surface would be required. In essence, this type of end cap would act as a molecular aligator clip. A potential linker of this type is the 9,10-phenanthroline moiety.[18,39] We have previously reported syntheses of phenanthrolinoporphyrins **11b** from tripyrranes, such as **34**, which are ultimately derived from 5-nitro-1,10-phenanthroline.[18,40] In order to investigate the feasibility of introducing a phenanthroline 'aligator clip' onto a pyrenoporphyrin, phenanthroline fused tripyrrane **34** was condensed with **29** under the '3+1' conditions to give the mixed ring fused porphyrin **35** (Scheme 7). Following purification on a grade 3 alumina column and recrystallization from chloroform–methanol, the phenanthroline fused pyrenoporphyrin **35** was isolated in 50% yield. Hence, this methodology is well suited to the introduction of mixed units of this type.

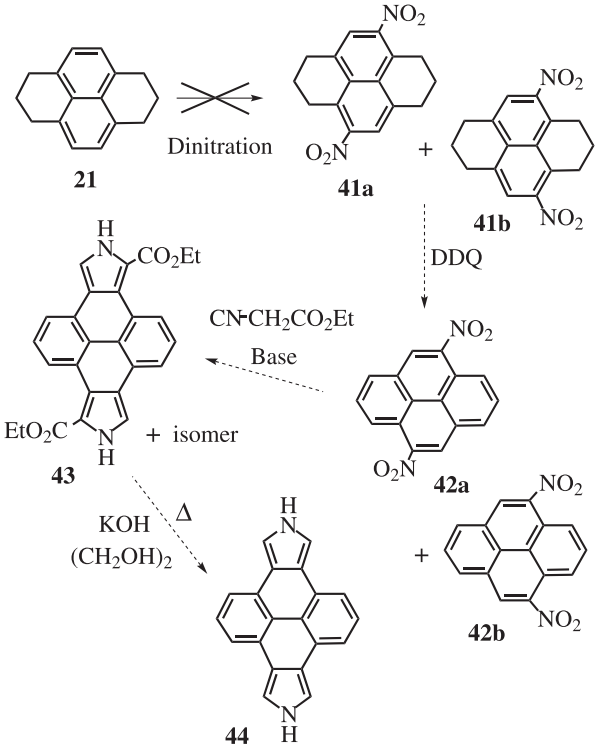
The synthesis of an *adj*-dipyrenoporphyrin was carried out using the '2+2' MacDonald approach (Scheme 8). Ethyl ester **16** was reacted with dimethoxymethane in the presence of catalytic *p*-toluenesulfonic acid to afford a virtually quantitative yield of the corresponding dipyrrylmethane **36**. This was heated with KOH in ethylene glycol at 190 °C under nitrogen for 30 min to cleave the



Scheme 8.

ester moieties. The crude product was then reacted with dialdehyde **37** in the presence of *p*-toluenesulfonic acid, and stirred for a further two days open to the air with excess zinc acetate to convert the initially formed porphodimethene intermediate **38** into the *adj*-dipyrenoporphyrin **39a**.[41,42] Again, the dimethyl ester had poor solubility characteristics and transesterification with isobutyl alcohol was necessary to form a reasonably soluble product. Following purification, *adj*-dipyrenoporphyrin **39b** was isolated in 53% yield. Small samples of the nickel(II), copper(II), and zinc complexes **40** for this system were also prepared.

Although it should be possible to dinitrate hexahydropyrene **21** to produce two isomeric compounds **41a** and **41b** (Scheme 9), this chemistry has so far failed in our hands and the presence of excess copper(II) nitrate lead to decomposition rather than required products. However, if this problem can be overcome, these could be dehydrogenated to give the fully unsaturated dinitropyrenes **42** and further reaction with phosphazene **23** and ethyl isocyanoacetate would give a mixture of two dipyrrolic regioisomers **43a** and **43b**. However, upon deprotection with KOH in refluxing ethylene glycol, a single dipyrrole **44** would be produced, and this hexacyclic system will be a suitable precursor for the synthesis of porphyrin dimers and related oligomers linked by pyrene moieties. Nevertheless, solubility issues will need to be addressed if these products are to be isolated and characterized.



Scheme 9.

2.2. Electronic absorption spectra of pyrenoporphyrins and related systems

In our earlier work in this area, we had anticipated that significant bathochromic shifts would be produced in π-extended porphyrin systems. However, in many cases the UV–vis absorption spectra are not significantly altered, although acenaphthoporphyrins, benzothiadiazoloporphyrins and related systems have proven to be exceptions.[43] The UV–vis spectra for monopyrenoporphyrins **15a** and **15b** showed moderate shifts compared to phenanthroporphyrins **11a**.[17] In 1% Et_3N–chloroform, **15a** gave a Soret band at 420 nm, and Q band absorptions at 517, 556, 581, and 638 nm (Fig. 1). The corresponding absorptions for phenanthroporphyrin **11a** were reported at 417, 516, 553, 577, and 634 nm

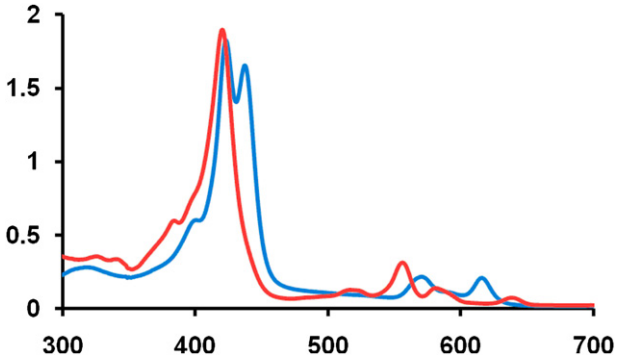


Figure 1. UV–vis spectra of pyrenoporphyrin **15a** in 1% Et_3N–chloroform (free base, red line) and 1% TFA–chloroform (dication **15a**H_2^{2+}, blue line).

(Table 1).[17c] In 1% TFA–chloroform, the corresponding dication **15a**H_2^{2+} was generated and this showed a split Soret band at 423 and 437 nm and two longer wavelength absorptions at 570 and 616 nm (Fig. 1); the values reported for **11a**H_2^{2+} were 403, 420, 566,

Table 1
Wavelength values for the Soret and Q bands of phenanthroporphyrin **11a** and pyrenoporphyrins in 1% Et_3N–chloroform

Porphyrin	Soret band	Q band IV	Q band III	Q band II	Q band I
11a	417 nm	516 nm	553 nm	577 nm	634 nm
15a	420 nm	517 nm	556 nm	581 nm	638 nm
15b	420 nm	517 nm	556 nm	581 nm	639 nm
32b	428 nm	—	578 nm	594 nm	—
39b	440 nm	537 nm	574 nm	596 nm	655 nm
35	431 nm	—	580 nm	604 nm	—

and 612 nm (Table 2).[17c] These shifts are modest in most cases, although a somewhat larger bathochromic shift is noted for the Soret bands of dication **15a**H_2^{2+} compared to **11a**H_2^{2+} (Table 2). The *opp*-dipyrenoporphyrin **32b** gave a strong Soret band at 428 nm;

Table 2
Wavelength values for the Soret and Q bands of phenanthroporphyrin dication **11a**H_2^{2+} and pyrenoporphyrins dications in 1% TFA–chloroform

Porphyrin dication	Soret bands	β band	α band
11aH_2^{2+}	403, 420 nm	566 nm	612 nm
15aH_2^{2+}	423, 437 nm	570 nm	616 nm
15bH_2^{2+}	423, 437 nm	571 nm	616 nm
32bH_2^{2+}	436, 453 nm	593 nm	643 nm
39bH_2^{2+}	449 nm	589 nm	637 nm

although four Q bands can be discerned, only the absorptions at 578 and 594 were prominent in this spectrum (Fig. 2; Table 1). This type of spectrum was also noted for an *opp*-diphenanthroporphyrin, which gave a Soret band at 429 and Q absorptions at 573 and 591 nm.[17] These values were again only shifted to longer wavelength in **32b** by 1–5 nm. A similar UV–vis spectrum was obtained for the mixed annelated porphyrin **35** and for *opp*-diphenanthrolinoporphyrins.[18] However, the dication for **32b** in 1% TFA–chloroform gave more significant shifts with a split somewhat weakened Soret absorption at 436 and 453 nm, and longer wavelength bands at 593 and 643 nm (Fig. 2; Table 2). In contrast, the *opp*-diphenanthroporphyrin system gave a single stronger Soret

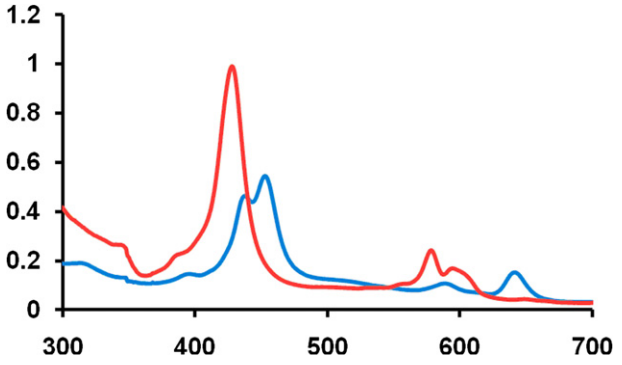


Figure 2. UV–vis spectra of *opp*-dipyrenoporphyrin **32b** in 1% Et_3N–chloroform (free base, red line) and 1% TFA–chloroform (dication **32b**H_2^{2+}, blue line).

band at 448 nm and Q bands at 583 and 632 nm. The *adj*-dipyrenoporphyrin **39b** gave a Soret band at 440 nm and Q bands at 537, 574, 596, and 655 nm (Fig. 3; Table 1); the analogous diphenanthroporphyrin showed similar absorptions at 434, 538, 571, 593, and 651 nm.[17] In 1% TFA–chloroform, dication **39b**H_2^{2+} gave a dominant Soret band at 449 nm and minor bands were observed at 589 and 637 nm (Fig. 3; Table 2). The *adj*-diphenanthroporphyrin dication gave a rather different spectrum with a split Soret band at 436 and 458 nm, and longer wavelength bands at 581 and 638 nm.[17] Overall, the electronic absorption properties are broadly similar to the related phenanthroporphyrins[17] and naphthoporphyrins,[15] although fairly consistent small bathochromic shifts were observed in these studies.

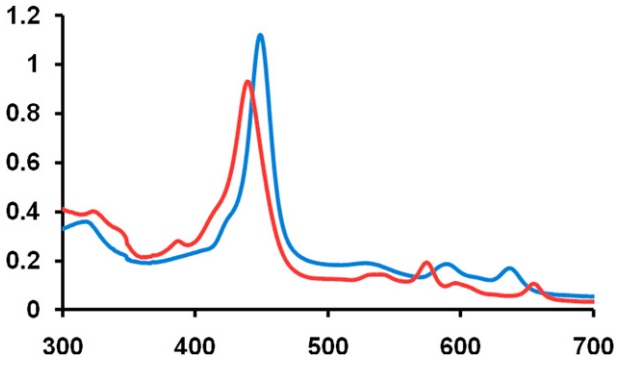


Figure 3. UV–vis spectra of *adj*-dipyrenoporphyrin **39b** in 1% Et_3N–chloroform (free base, red line) and 1% TFA–chloroform (dication **39b**H_2^{2+}, blue line).

The same trends were noted for the metallo-derivatives of pyrenoporphyrins. In previous studies, the nickel(II), copper(II), and zinc complexes of π-extended porphyrins showed bathochromic shifts with increasing atomic number.[31,43] This is also the case for metallo-pyrenoporphyrins **28a**–**c** (Table 3). The nickel(II) complex **28a** gave a Soret band at 419 nm and α and β bands at 581 and 537 nm, respectively. These absorptions were observed at 422, 588, and 543 nm for copper(II) complex **28b**, and 428, 595, and 553 nm for zinc complex **28c**. These values were all slightly red shifted by 3–10 nm compared to the corresponding metallo-derivatives for phenanthroporphyrin **11a**.[17] However, the metal complexes were only sparingly soluble in chloroform, although the solubility of **28c** was greatly improved in the presence of pyrrolidine. This is due to coordination of the secondary amine to the zinc porphyrin inhibiting aggregation of these highly conjugated macrocycles. However, this also causes the UV–vis absorption bands to shift to 444, 603, and 562 nm (Table 3). The UV–vis spectra for the metal complexes derived from *opp*- and *adj*-dipyrenoporphyrins **32b** and **39b** were also very similar to spectra obtained for the analogous complexes of diphenanthroporphyrins and while all of the bands were bathochromically shifted, these shifts were all less than 10 nm.

Table 3
Wavelength values for the Soret and Q bands of metallo-derivatives of pyrenoporphyrins in chloroform. In each case, derivative a is the nickel(II) complex, derivative b is the copper(II) complex and derivative c is the zinc complex. The data for the zinc chelates in 1% pyrrolidine are also provided

Metalloporphyrin	Soret band	β band	α band
28a	419 nm	537 nm	581 nm
28b	422 nm	543 nm	588 nm
28c	428 nm	553 nm	595 nm
28c in 1% pyrrolidine	444 nm	562 nm	603, 672 nm
33a	434 nm	—	609 nm
33b	434 nm	—	615 nm
33c	454 nm	576 nm	626 nm
33c in 1% pyrrolidine	455 nm	577 nm	628 nm
40a	436 nm	556 nm	599 nm
40b	438 nm	562 nm	605 nm
40c	446 nm	572 nm	613 nm
40c in 1% pyrrolidine	461 nm	578 nm	619 nm

2.3. NMR spectra of pyrenoporphyrins and related systems

The porphyrin products were all characterized by UV–vis spectroscopy, fast atom bombardment mass spectrometry and, with the exception of the paramagnetic copper(II) complexes, by NMR spectroscopy. In general, the proton NMR spectra of porphyrins show the presence of a large diatropic ring current that are usually attributed to the presence of diaza[18]annulene substructures.[44] These usually shift the NH resonances upfield to near −4 ppm, while the *meso*-protons appear downfield at 10 ppm.[44,45] Methyl groups attached to the porphyrin system are indirectly effected by the powerful diamagnetic ring current and commonly appear at 3.6 ppm. The proton NMR spectra of pyrenoporphyrins clearly demonstrate that the introduction of fused pyrene units does not interfere with the diatropic characteristics of the porphyrin nucleus. For instance, **15a** showed the NH resonance at −3.8 ppm, while the *meso*-protons were observed as two 2H singlets at 9.9 and 10.9 ppm; the latter resonance is further deshielded by the adjacent fused pyrene unit. The methyl substituents also gave rise to a 6H singlet at 3.6 ppm. Addition of a drop of TFA to the NMR tube gave the dication **15a**H_2^{2+}, and this showed a significant downfield shift for the external *meso*-protons giving two 2H singlets at 10.5 and 11.6 ppm. The four internal NHs gave rise to three broad upfield resonances at −2.1 (2H), −2.7 (1H), and −3.1 ppm (1H). These data demonstrate that the aromatic ring current is essentially just as strong for the dication as for the free base, and also show that there are significant variations in the environment within the porphyrin cavity of **15a**H_2^{2+}. The proton NMR spectra for the free base and diprotonated forms of **15a** also confirm the presence of a plane of symmetry. Similar NMR data were obtained for diester **15b**. The carbon-13 NMR spectra for **15a** and **15b** were also obtained in TFA–$CDCl_3$, and these show the expected number of carbon resonances for structure possessing a plane of symmetry. The *meso*-carbons of porphyrins appear near 100 ppm, and these resonances have been shown to be very sensitive for establishing the isomeric purity of porphyrin samples.[45] As expected, pyrenoporphyrins **15a** and **15b** both only showed two resonances for the *meso*-carbons; for **15b**H_2^{2+} these were observed at 98.6 and 100.6 ppm (Fig. 4). The *opp*- and *adj*-dipyrenoporphyrins were also characterized in the same way, although only poor quality spectra could be obtained for the free base forms of **32b** and **39b** due to low solubility. However, in TFA–$CDCl_3$ well resolved proton and carbon-13 NMR spectra were obtained. The carbon-13 NMR spectrum of **32b**H_2^{2+} showed two resonances for the *meso*-carbons at 100.3 and

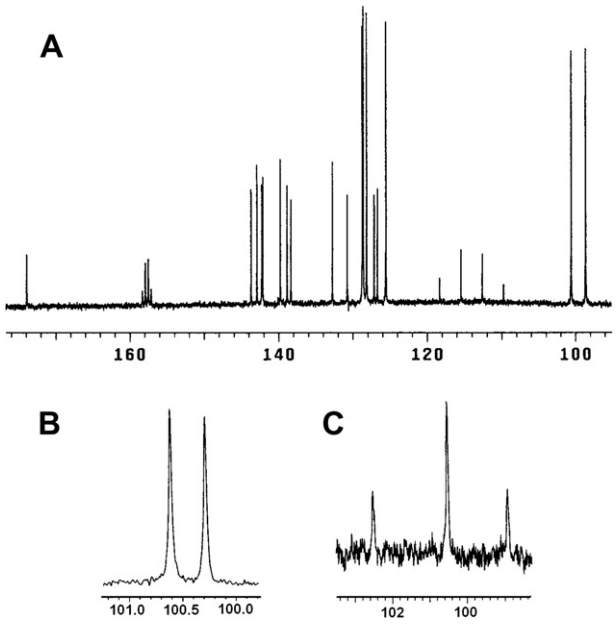


Figure 4. Partial 100 MHz carbon-13 NMR spectra of pyrenoporphyrins in TFA–$CDCl_3$. A. Spectrum for monopyrenoporphyrin **15b**H_2^{2+} showing two resonances for the *meso*-carbons near 100 ppm. B. *meso*-carbon region for *opp*-dipyrenoporphyrin **32b**H_2^{2+} showing two resonances as would be expected for a porphyrin species of this type with a plane of symmetry. C. *meso*-carbon region for *adj*-dipyrenoporphyrin **39b**H_2^{2+} showing three separate resonances.

100.6 ppm, again confirming the presence of a plane of symmetry (Fig. 4). Although *adj*-dipyrenoporphyrin **39b**H_2^{2+} also has a plane of symmetry, this bisects two of the *meso*-carbons and for this reason the carbon-13 NMR spectrum shows three *meso*-carbon resonances at 98.9, 100.5, and 102.5 ppm (Fig. 4). The mixed phenanthroline-pyrene fused porphyrin **35** was only sufficiently soluble in the presence of TFA for NMR data to be collected. However, this gave well resolved proton and carbon-13 NMR spectra in TFA–$CDCl_3$ that confirmed the presence of a plane of symmetry. As expected, in the carbon-13 NMR spectrum the *meso*-carbons gave rise to only two resonances at 100.0 and 100.4 ppm.

The nickel(II) complexes gave poor quality NMR spectra due to their low solubility, but these were consistent with the expected structures. The zinc complexes also gave poor quality spectra in $CDCl_3$, but after addition of a drop of pyrrolidine to the NMR tube well resolved spectra could be obtained. The *meso*-protons for zinc pyrenoporphyrin **28a** in trace pyrrolidine–$CDCl_3$ gave two 2H singlets at 10.0 and 11.3 ppm, while the pyrene unit gave resonances at 8.3 (2H, s), 8.4 (2H, d), 8.5 (2H, t), and 10.5 ppm (2H, d). These data again confirmed the retention of a strong diamagnetic ring current and a plane of symmetry for these derivatives. Similar results were obtained for the dipyrenoporphyrin zinc complexes **28c** and **40c**.

3. Conclusions and future prospects

Barton–Zard condensation of 4-nitropyrene with ethyl isocyanoacetate in the presence of a phosphazine base gave excellent yields of a pyrenopyrrole ethyl ester, and this precursor was used to synthesize mono-, *opp*-di- and *adj*-dipyrenoporphyrins. In addition, a phenanthroline derived tripyrrane was used to prepare a porphyrin with fused pyrene and phenanthroline moieties. These novel porphyrins were obtained in good yields and possess the required geometries for the construction of molecule wires. Furthermore, phenanthroline could act as a molecular aligator clip or connector for systems of that type. However, several problems will have to be overcome to generate pyrene linked porphyrin chains or networks. The low solubility of dipyrenoporphyrins will necessitate the introduction of bulky substituents that can block aggregation of these high molecular weight species. In this regard, 2,7-di-*tert*-butylpyrene **33** may prove to be a useful starting material for these investigations as the *tert*-butyl substituents will greatly increase the solubility of these porphyrins. The dinitration of hexahydropyrenes will also need to be addressed before the dipyrrolopyrenes needed for oligoporphyrin chain formation can be formed by the Barton–Zard methodology. Nevertheless, these preliminary results suggest that this approach may lead to a new family of conjugated oligoporphyrins with the potential to act as molecular wires.

4. Experimental section

4.1. General methods

Acetoxymethylpyrroles **25a**[18] and **25b**,[46] hexahydropyrene **21**,[36] ethyl isocyanoacetate,[47] and dialdehydes **27**[45,48] and **37**[49] were synthesized by literature procedures. Phosphazene **23** was purchased from Fluka; pyrene, DBU, *p*-toluenesulfonic acid, DDQ, acetic anhydride, copper(II) nitrate, copper(II) acetate, nickel(II) acetate, and zinc acetate were purchased from Aldrich or Acros. UV–vis spectra were obtained on a Carey spectrophotometer. NMR spectra were recorded on a Varian Gemini-400 MHz NMR spectrometer at 25 °C, unless otherwise indicated, and recorded in parts per million relative to $CDCl_3$ (residual chloroform at δ=7.26 ppm) in proton NMR and the $CDCl_3$ triplet at δ=77.23 ppm in carbon-13 NMR spectra. Mass spectroscopic data were obtained from the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, and elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

4.2. Synthetic procedures

*4.2.1. 4-Nitropyrene (**17**).* A solution of copper(II) nitrate (2.319 g) in acetic anhydride (225 mL) was added to a stirred solution of 1,2,3,6,7,8-hexahydropyrene (2.00 g, 9.61 mmol) in acetic anhydride (400 mL) over a period of 1 h and the mixture was allowed to stir at room temperature under nitrogen for a further 7 h. Following this, the reaction mixture was poured into 1200 g of ice containing 2 M sulfuric acid (20 mL). After stirring for 15 h, the mixture was extracted with dichloromethane and washed with water, sodium bicarbonate solution, 5% sodium hydroxide and water. It was dried over sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on silica eluting with 4:1 hexanes–dichloromethane to yield the reduced nitropyrene **22** (1.50 g, 5.93 mmol, 62%) as yellow crystals, mp 85–86 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.01–2.09 (4H, m), 3.06–3.12 (6H, m), 3.30 (2H, t, J=6.3 Hz), 7.26 (1H, dt, J=1.0, 7.2 Hz), 7.29 (1H, dt, J=1.0, 7.2 Hz), 7.64 (1H, t, J=1.1 Hz); ^{13}C NMR ($CDCl_3$): δ 22.8, 23.0, 28.2, 31.1, 31.3, 31.5, 118.1, 125.8, 127.1, 130.3, 130.8, 132.0, 134.8, 136.2, 136.8, 145.1. The nitro-hexahydropyrene (3.25 g; 12.8 mmol) was dissolved in toluene (300 mL), DDQ (10.25 g; 44 mmol) was added and the solution refluxed overnight. The resulting dark green colored mixture was then poured into hexanes (615 mL) to precipitate out the hydroquinone by-product. The upper layer was decanted and evaporated to dryness. The residue was then chromatographed on silica, eluting with 4:1 hexanes–dichloromethane, to yield a yellow solid. Recrystallization from acetonitrile–water afforded **17** (2.21 g, 8.95 mmol, 70%) as bright yellow crystals, mp 184–185 °C (lit. mp[39] 185–186 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–8.08 (3H, m), 8.11 (1H, t, J=7.8 Hz), 8.25–8.32 (3H, m), 8.81 (1H, s), 8.86 (1H, d,

J=8.2 Hz); ^{13}C NMR ($CDCl_3$): δ 121.9, 122.5, 125.62, 125.64, 126.8, 127.09, 127.13, 127.4, 128.0, 128.1, 128.3, 128.8, 131.3, 134.4, 146.4.

*4.2.2. Ethyl pyreno[4,5-c]pyrrole-1-carboxylate (**16**).* Phosphazene base **23** (1.77 g, 97%, 5.50 mmol) was added dropwise to a stirring solution of 4-nitropyrene (1.23 g, 4.98 mmol) and ethyl isocyanoacetate (0.70 g, 6.2 mmol) in THF (40 mL) (freshly distilled from calcium hydride) and stirred overnight at room temperature. The solution was diluted with chloroform, washed with water and evaporated under reduced pressure. The residue was then chromatographed on silica, eluting with dichloromethane. Recrystallization from dichloromethane–hexanes afforded the pyrenopyrrole ester (1.42 g, 4.54 mmol, 91%) as a pale yellow solid, mp 157–158 °C; IR (Nujol mull): ν 3272 (NH str.), 1656 cm^{-1} (C=O str.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (3H, t, J=7 Hz), 4.53 (2H, q, J=7 Hz), 7.87 (1H, t, J=7.6 Hz), 7.92–8.03 (4H, m), 8.11 (1H, d, J=8 Hz), 8.30 (1H, d, J=8 Hz), 10.01 (1H, br s), 10.06 (1H, d, J=8 Hz); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.43 (3H, t, J=7 Hz), 4.44 (2H, q, J=7 Hz), 7.93 (1H, t, J=7.6 Hz), 7.97 (1H, t, J=7.6 Hz), 8.02–8.08 (3H, m), 8.17 (1H, d, J=7.2 Hz), 8.41 (1H, d, J=3.2 Hz), 8.60 (1H, d, J=7.2 Hz), 10.04 (1H, d, J=7.6 Hz), 12.91 (1H, br s); ^{13}C NMR (DMSO-d_6): δ 14.7, 60.3, 116.0, 118.3, 120.0, 121.9, 122.6, 123.4, 124.2, 124.5, 125.3, 126.1, 126.5, 126.7, 127.0, 127.2, 127.9, 131.4, 131.5, 160.9; EI-MS (70 eV): m/z (% rel int.) 314 (10), 313 (45, M^+), 268 (25), 267 (100, $[M-EtOH]^+$), 240 (12), 239 (28), 238 (23), 213 (21), 173 (18). Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.23; H, 4.90; N, 4.57.

*4.2.3. Pyreno[4,5-c]pyrrole (**24**).* Nitrogen gas was bubbled through a mixture of pyrenopyrrole ester **16** (0.500 g, 1.60 mmol) and potassium hydroxide (1.00 g, 87%, 15 mmol) in ethylene glycol (20 mL) for 5 min. Hydrazine (20 drops) was then added and the mixture was stirred under reflux in a preheated oil bath for 1 h. The hot reaction mixture was then poured into ice-water, and the resulting greenish precipitate was collected by suction filtration, washed with water and dried under vacuum overnight. The pyrenopyrrole (380 mg, 1.58 mmol, 98%) was obtained as a light green powder, mp >300 °C, dec; IR (Nujol mull): 3391 cm^{-1} (NH str); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.84 (2H, t, J=7.6 Hz), 7.94–7.97 (6H, m), 8.38 (2H, d, J=8.0 Hz), 12.01 (1H, br s); ^{13}C NMR (DMSO-d_6): δ 112.5, 119.4, 120.5, 123.5, 124.1, 126.8, 127.9, 128.9, 132.2; EI-MS (70 eV): m/z (% rel int.) 242 (21), 241 (100, M^+), 240 (29), 213 (22). HRMS (EI), m/z calcd for $C_{18}H_{11}N$: 241.0891. Found: 241.0895. Anal. Calcd for $C_{18}H_{11}N\cdot{}^1/_3H_2O$: C, 87.42; H, 4.75; N, 5.66. Found: C, 87.14; H, 4.41; N, 5.74.

*4.2.4. Pyreno[4,5-c]pyrrole-1-carbaldehyde (**30**).* DMF (1.2 g, 16 mmol) was cooled in a salt-ice bath to 0 °C and $POCl_3$ (3.1 g, 20 mmol) added dropwise while maintaining the internal temperature between 10–15 °C. An exothermic reaction occurred with the formation of the Vilsmeier complex. The ice bath was removed and the reaction mixture was allowed to stir at room temperature for 15 min. Dichloromethane (40 mL) was then added and the flask was cooled to 0 °C. A solution of pyrenopyrrole **24** (0.600 g, 2.49 mmol) in dichloromethane (40 mL) was then added over a period of 40 min. The salt-ice bath was then replaced with a hot water bath and the mixture refluxed for 15 min. The flask was then cooled to 30–32 °C, sodium acetate trihydrate (15 g) in 28 mL of water was added dropwise and the reaction mixture refluxed for an additional 15 min. The two layers were separated and the aqueous layers extracted with chloroform. The combined organic layers were dried over sodium sulfate and evaporated under reduced pressure. Recrystallization from chloroform–hexanes gave the aldehyde **30** (450 mg, 1.67 mmol, 67%) as a dark brown solid, mp 210 °C; IR (Nujol mull): 3230 (NH str.), 1620 cm^{-1} (C=O str); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (1H, t, J=7.8 Hz), 8.01 (1H, t, J=7.8 Hz), 8.08–8.13 (3H, m), 8.23 (1H, d, J=7.6 Hz), 8.63 (1H, d, J=7.0 Hz), 8.67 (1H, d, J=3.2 Hz), 9.52 (1H, br d), 10.31 (1H, s), 13.43 (1H, br s); ^{13}C NMR (DMSO-d_6): δ 120.4, 122.1, 122.5, 122.6, 124.1, 124.5, 124.7, 124.8, 126.47, 126.51, 126.7, 126.8, 127.4, 127.7, 127.8, 131.5, 131.6, 178.9; EI-MS (70 eV): m/z (% rel int.) 270 (21), 269 (100, M^+), 241 (64, $[M-CO]^+$), 240 (37), 213 (34). HRMS (EI), m/z calcd for $C_{19}H_{11}NO$: 269.0841. Found: 269.0844. Anal. Calcd for $C_{19}H_{11}NO\cdot{}^1/_4CHCl_3$: C, 77.29; H, 3.79; N, 4.68. Found: C, 77.49; H, 3.76; N, 4.97.

*4.2.5. 1-(2-Cyano-2-ethoxycarbonylvinyl)pyreno[4,5-c]pyrrole (**31**).* Pyrrolealdehyde **30** (450 mg, 1.67 mmol), ethyl cyanoacetate (550 mg, 4.8 mmol), and piperidine (12 drops) were refluxed in ethanol (28 mL) for 4 h. The reaction mixture was cooled to room temperature, and the precipitate suction filtered and dried under vacuum overnight to give the protected aldehyde as golden yellow crystals (380 mg, 1.04 mmol, 63%), mp 219–220 °C, dec; IR (Nujol mull): 3332 (NH str.), 2201 (CN str), 1712 cm^{-1} (C=O str); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.35 (3H, t, J=7.2 Hz), 4.35 (2H, q, J=7.2 Hz), 8.00 (1H, t, J=7.6 Hz), 8.06 (1H, t, J=7.8 Hz), 8.11 (2H, s), 8.16 (1H, d, J=7.8 Hz), 8.24 (1H, d, J=7.8 Hz), 8.49 (1H, d, J=7.8 Hz), 8.66 (1H, d, J=7.6 Hz), 8.77 (1H, s), 8.96 (1H, s), 12.58 (1H, br s); ^{13}C NMR (DMSO-d_6): δ 14.4, 61.9, 91.8, 117.6, 120.6, 121.3, 122.3, 122.6, 123.0, 124.9, 125.1, 125.9, 126.2, 126.38, 126.43, 126.6, 126.9, 127.7, 128.4, 129.1, 131.5, 132.0, 141.3, 163.8; EI-MS (70 eV): m/z (% rel int.) 366 (21), 365 (27), 364 (100, M^+), 337 (21, $[M-HCN]^+$), 318 (71, $[M-EtOH]^+$), 291 (94, $[M-CO_2Et]^+$). HRMS (EI), m/z calcd for $C_{24}H_{16}N_2O_2$: 364.1212. Found: 364.1210. Anal. Calcd for $C_{24}H_{16}N_2O_2\cdot{}^1/_4H_2O$: C, 78.14; H, 4.51; N, 7.59. Found: C, 77.93; H, 4.26; N, 7.54.

*4.2.6. Pyreno[4,5-c]pyrrole-1,3-dicarbaldehyde (**29**).* A second formylation reaction was carried out on the protected aldehyde **31** (380 mg, 1.04 mmol) following the procedure used for **30**. The resulting crude aldehyde was then refluxed in 3 M sodium hydroxide (21 mL) for 30 min. The solution was cooled to room temperature and neutralized with dilute sulfuric acid. The resulting dark brown precipitate was suction filtered, washed with water and dried in vacuo overnight. The dialdehyde (335 mg, quantitative) was sufficiently pure to be used without further purification. Mp >300 °C, dec; IR (Nujol mull): 1659 cm^{-1} (C=O str); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02 (2H, t, J=7.8 Hz), 8.11 (2H, s), 8.25 (2H, d, J=7.6 Hz), 9.51 (2H, d, J=7.6 Hz), 10.47 (2H, s), 14.38 (1H, br s); ^{13}C NMR (DMSO-d_6): δ 124.0, 124.6, 124.7, 125.6, 126.6, 126.8, 127.6, 130.7, 131.2, 182.1; EI-MS (70 eV): m/z (% rel int.) 298 (22), 297 (100, M^+), 296 (3.8), 269 (25, $[M-CO]^+$), 268 (33, $[M-CHO]^+$), 241 (38, $[M-2CO]^+$), 213 (36). HRMS (EI), m/z calcd for $C_{20}H_{11}NO_2$: 297.0790. Found: 297.0788. Anal. Calcd for $C_{20}H_{11}NO_2\cdot{}^1/_2H_2O$: C, 78.42; H, 4.06; N, 4.57. Found: C, 78.14; H, 3.83; N, 5.02.

*4.2.7. Diethyl 1,1′-(dipyreno[4,5-c]pyrrolyl)methane-3,3′-dicarboxylate (**36**).* Ethyl pyreno[4,5-*c*]pyrrole-1-carboxylate (**16**; 900 mg, 2.87 mmol), dimethoxymethane (306 mg, 4.0 mmol), and *p*-toluenesulfonic acid (135 mg) were dissolved in 180 mL of glacial acetic acid. The reaction vessel was purged with nitrogen, and the mixture was stirred under an atmosphere of nitrogen at room temperature for four days. The mixture was poured into ice-water and allowed to stand for 2 h. The resulting precipitate was filtered, washed with water and dried in vacuo to give the dipyrrylmethane (895 mg, 1.40 mmol, 98%) as a purple powder, mp >300 °C. An analytical sample was obtained by recrystallization from THF–hexanes as a pale purple colored powder, mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.13 (6H, t, J=7.0 Hz), 4.28 (4H, q, J=7.0 Hz), 5.73 (2H, s), 7.76 (2H, t, J=7.8 Hz), 7.97 (2H, t, J=7.8 Hz), 8.04–8.11 (6H, m), 8.19 (2H, d, J=7.2 Hz), 8.47 (2H, d, J=7.6 Hz), 10.00 (2H, d, J=7.6 Hz), 12.01 (2H, br s); ^{13}C NMR (DMSO-d_6): δ 14.8, 60.9, 114.9, 118.7, 121.3,

123.8, 125.0, 125.3, 125.7, 126.7, 126.9 (2), 127.0, 127.8, 127.9, 128.0, 128.4, 131.9, 132.1, 161.1. Anal. Calcd for $C_{43}H_{30}N_2O_4$: C, 80.86; H, 4.73; N, 4.39. Found: C, 80.49; H, 4.97; N, 4.30.

*4.2.8. 1,3-Bis(5-tert-butoxycarbonyl-3-butyl-4-methyl-2-pyrrolylmethyl)pyreno[4,5-c]pyrrole (**26a**).* Acetic acid was added to a mixture of pyrenopyrrole **24** (106 mg, 0.44 mmol) and acetoxymethylpyrrole **25a** (289 mg, 0.93 mmol) in ethanol (10 mL), and the resulting mixture refluxed with stirring under a nitrogen atmosphere overnight. The solution was cooled and poured into 60 mL of ice-water. The resulting precipitate was suction filtered to give the tripyrrane (197 mg, 0.27 mmol, 61%) as a pink powder, mp 150 °C, dec; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (6H, t, J=7.2 Hz), 1.24–1.40 (8H, m), 1.48 (18H, s), 2.29 (6H, s), 2.33 (4H, t, J=7.0 Hz), 4.52 (4H, s), 7.83 (2H, t, J=7.6 Hz), 7.93–7.96 (4H, doublet overlapping with singlet), 7.99 (1H, br s), 8.20 (2H, d, J=7.6 Hz), 8.52 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.9, 14.1, 22.8, 23.9, 26.7, 28.7, 33.2, 80.6, 116.4, 119.6, 119.7, 120.4, 123.4, 124.1, 124.7, 126.2, 126.6, 127.5, 127.7, 129.4, 132.3, 161.2. Anal. Calcd for $C_{48}H_{57}N_3O_4$: C, 77.91; H, 7.76; N, 5.68. Found: C, 77.44; H, 7.72; N, 5.76.

*4.2.9. 1,3-Bis(5-tert-butoxycarbonyl-3(2-methoxycarbonylethyl)-4-methyl-2-pyrrolylmethyl)pyreno[4,5-c]pyrrole (**26b**).* Nitrogen gas was bubbled through a mixture of pyrenopyrrole **24** (100 mg, 0.415 mmol) and acetoxymethylpyrrole **25b** (280 mg, 0.83 mmol) in 2-propanol (3 mL) and glacial acetic acid (1 mL) for 10 min. The resulting mixture was stirred under reflux overnight, poured into ice, and the precipitated solid filtered and dried under vacuum to give the tripyrrane (238 mg, 0.30 mmol, 72%) as a brown powder, mp 96–98 °C, dec. The precipitated product was reasonably pure by NMR spectroscopy, and was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (18H, s), 2.26 (6H, s), 2.46 (4H, t, J=7.2 Hz), 2.77 (4H, t, J=7.2 Hz), 3.53 (6H, s), 4.62 (1H, s), 7.81 (2H, t, J=7.6 Hz), 7.92–7.94 (4H, m), 8.25 (2H, d, J=7.6 Hz), 8.73 (2H, br s), 9.11 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.7, 19.6, 26.4, 28.6, 34.9, 51.7, 80.6, 116.8, 119.8, 119.9, 120.1, 120.5, 124.2, 124.8, 126.2, 126.3, 127.7, 129.0, 129.3, 132.4, 161.0, 174.0. HRMS (EI), m/z calcd for $C_{48}H_{53}N_3O_8$: 799.3832. Found: 799.3832. Anal. Calcd for $C_{48}H_{53}N_3O_8 \cdot {}^1/_2H_2O$: C, 71.27; H, 6.73; N, 5.20. Found: C, 70.98; H, 6.65; N, 5.27.

*4.2.10. 1,14-Bis(5-tert-butoxycarbonyl)-3,12-bis(2-methoxycarbonylethyl)-2,13-dimethyl-5,16-dihydropyreno[4,5-g]tripyrrin (**26c**).* Attempts to purify the foregoing compound (60 mg, 0.075 mmol) on a silica column, eluting with chloroform, gave a dark orange colored band. Crystallization from ethanol gave the title tripyrrene (27 mg, 0.034 mmol, 45%) as bright orange crystals, mp 193.5–195 °C; UV–vis (CH_2Cl_2): λ_{max} ($\log_{10}\varepsilon$) 475 nm (4.59); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (18H, s), 2.30 (3H, s), 2.34 (3H, s), 2.61 (2H, t, J=7.8 Hz), 2.66 (2H, t, J=7.2 Hz), 3.01 (2H, t, J=7.6 Hz), 3.12 (2H, t, J=7.2 Hz), 3.66 (3H, s), 3.69 (3H, s), 4.77 (2H, s), 7.98 (1H, t, J=7.8 Hz), 8.04–8.08 (2H, AB quartet, J=9.2 Hz), 8.09 (1H, s), 8.14–8.18 (2H, 2 overlapping doublets), 8.24 (1H, d, J=7.6 Hz), 8.49 (1H, d, J=8.0 Hz), 8.83 (1H, br s), 8.97 (1H, d, J=8.0 Hz), 12.09 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.3, 10.8, 20.1, 28.5, 28.6, 32.0, 35.2, 35.7, 51.8, 52.0, 80.3, 81.4, 119.9, 120.7, 121.2, 121.3, 122.1, 125.2, 125.8, 125.9, 126.0, 126.4, 126.5, 126.6, 126.9, 127.1, 127.3, 127.4, 128.08, 128.11, 130.5, 131.8, 131.9, 132.2, 132.5, 138.1, 147.5, 160.4, 161.0, 167.0, 173.4, 173.7. HRMS (EI), m/z calcd for $C_{48}H_{51}N_3O_8$: 797.3676. Found: 797.3678. Anal. Calcd for $C_{48}H_{51}N_3O_8$: C, 72.25; H, 6.44; N, 5.27. Found: C, 72.37; H, 6.52; N, 5.33.

*4.2.11. 7,18-Dibutyl-12,13-diethyl-8,17-dimethylpyreno[4,5-b]porphyrin (**15a**).* Tripyrrane **26a** (110 mg, 0.149 mmol) was stirred with TFA for 10 min under nitrogen. The solution was diluted with dichloromethane (19 mL), followed immediately by diformylpyrrole **27** (32.0 mg, 0.179 mmol), and the resulting mixture stirred for 2 h. Following neutralization of the solution by the dropwise addition of triethylamine, DDQ was added, and the mixture stirred for an additional 1 h. The mixture was diluted with chloroform, washed with water, and chromatographed on silica eluting with dichloromethane. Recrystallization from chloroform–methanol gave the pyrenoporphyrin (40 mg, 0.059 mmol, 40%) as purple crystals, mp 275 °C, dec; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 384 (4.80), 421 (5.30), 520 (3.99), 559 (4.55), 580 (4.20), 636 nm (3.51); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 389 (4.90), 421 (5.31), 435 (4.17), 570 (4.31), 617 nm (4.32); UV–vis (Ni(II) complex in $CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 419 (5.21), 537 (4.03), 584 nm (4.64); UV–vis (Cu(II) complex in $CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 421, 543, 588 nm; UV–vis (Zn complex in $CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 427 (5.17), 552 (4.02), 597 nm (4.97); ^{1}H NMR (400 MHz, $CDCl_3$): δ −3.78 (2H, br s), 1.19 (6H, t, J=7.4 Hz), 1.81 (4H, sextet, J=7.3 Hz), 1.94 (6H, t, J=7.8 Hz), 2.29 (4H, quintet, J=7.6 Hz), 3.59 (6H, s), 3.96–4.05 (8H, overlapping triplet and quartet), 8.26 (2H, s), 8.34–8.40 (4H, m), 9.95 (2H, s), 10.04 (2H, d, J=7.0 Hz), 10.91 (2H, s); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): δ −3.08 (1H, br s), −2.75 (1H, v br), −2.16 (2H, br s), 1.07 (6H, t, J=7.4 Hz), 1.66 (4H, sextet, J=7.4 Hz), 1.75 (6H, t, J=7.8 Hz), 2.15 (4H, quintet, J=7.4 Hz), 3.63 (6H, s), 4.09–4.19 (8H, overlapping triplet and quartet), 8.42 (2H, s), 8.67–8.71 (4H, m), 10.20–10.25 (2H, m), 10.53 (2H, s), 11.58 (2H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 12.3, 14.2, 17.6, 20.2, 23.3, 26.9, 34.6, 98.5, 100.1, 125.0, 127.0, 127.1, 128.1, 128.7, 130.4, 132.9, 137.6, 138.2, 142.2, 142.6, 142.7, 143.4, 143.6. HRMS (FAB), m/z calcd for $C_{48}H_{48}N_4$+H: 681.3957. Found: 681.3958. Anal. Calcd for $C_{48}H_{48}N_4$: C, 84.65; H, 7.12; N, 8.23. Found: C, 84.15; H, 6.83; N, 7.99.

*4.2.12. 12,13-Diethyl-7,18-bis(2-methoxycarbonylethyl)-8,17-dimethylpyreno[4,5-b]porphyrin (**15b**).* Nitrogen gas was bubbled through a pear shaped flask containing tripyrrane **26b** (150 mg, 0.188 mmol) and TFA (2 mL) for 10 min. Dichloromethane (38 mL) was added, followed by dialdehyde **27** (32.0 mg, 0.179 mmol), and the reaction mixture stirred under nitrogen in the dark for 3 h. The solution was washed with water, the aqueous solution back extracted with chloroform, and the combined organic layers shaken vigorously with a 0.1% ferric chloride solution for 10 min to bring about the oxidation. The solution was then washed with water, sodium bicarbonate solution, and water, and evaporated under reduced pressure. The residue was chromatographed on silica eluting with 50:50 chloroform–dichloromethane. Recrystallization from chloroform–methanol gave the pyrenoporphyrin **15b** (37 mg, 0.050 mmol, 28%) as dark purple crystals, mp 257–258 °C, dec; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 420 (5.23), 517 (3.95), 556 (4.41), 581 (4.01), 639 nm (3.66); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 423 (5.23), 437 (5.15), 571 (4.25), 616 nm (4.23); ^{1}H NMR (400 MHz, $CDCl_3$): δ −4.62 (2H, br s), 1.96 (6H, t, J=7.6 Hz), 2.97 (4H, br t), 3.37 (6H, s), 3.58 (6H, s), 3.88 (4H, br t), 4.00 (4H, br q, J=7.6 Hz), 8.19–8.24 (4H, overlapping doublet and singlet), 8.31 (2H, d, J=8.0 Hz), 9.57 (2H, d, J=7.2 Hz), 9.69 (2H, s), 10.13 (2H, s); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): δ −3.11 (1H, br s), −2.73 (1H, v br), −2.05 (2H, br s), 1.75 (6H, t, J=7.6 Hz), 3.22 (4H, t, J=7.2 Hz), 3.66 (6H, s), 3.68 (6H, s), 4.12 (4H, q, J=7.6 Hz), 4.49 (4H, t, J=7.0 Hz), 8.40 (2H, s), 8.67–8.74 (4H, m), 10.43 (2H, d, J=7.6 Hz), 10.55 (2H, s), 11.82 (2H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 12.2, 17.4, 20.1, 22.0, 35.5, 52.4, 98.6, 100.6, 125.5, 126.7, 127.1, 128.2, 128.6, 128.7, 130.7, 132.8, 138.4, 138.9, 139.8, 142.1, 142.3, 142.9, 143.7, 173.9. HRMS (FAB), m/z calcd for $C_{48}H_{44}N_4O_4$+H: 741.3441. Found: 741.3440. Anal. Calcd for $C_{48}H_{44}N_4O_4 \cdot {}^1/_8CHCl_3$: C, 76.48; H, 5.88; N, 7.41. Found: C, 76.41; H, 5.57; N, 7.21.

*4.2.13. 12,13-Diethyl-7,18-bis(2-methoxycarbonylethyl)-8,17-dimethylpyreno[4,5-b]porphyrinatonickel(II) (**28a**).* Pyrenoporphyrin **15b** (10.0 mg, 0.0135 mmol) and nickel(II) acetate tetrahydrate (17 mg, 0.068 mmol) were refluxed with DMF (10 mL) for 4 h. The mixture was diluted with chloroform, washed with water and

evaporated under reduced pressure. Recrystallization from chloroform–methanol gave the nickel(II) chelate (5.1 mg, 6.4×10^{-3} mmol, 47%) as purple crystals, mp 219–220 °C, dec; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 419 (5.13), 537 (3.98), 581 nm (4.55); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (6H, t, J=7.2 Hz), 3.08 (4H, br t), 3.36 (6H, s), 3.64 (6H, s), 3.90 (4H, q, J=7.2 Hz), 4.05 (4H, br t), 8.30 (2H, s), 8.37–8.43 (4H, m), 9.54 (2H, s), 9.59–9.64 (2H, br m), 10.35 (2H, br s). HRMS (FAB), m/z calcd for $C_{48}H_{42}N_4NiO_4$+H: 797.2638. Found: 797.2638.

*4.2.14. 12,13-Diethyl-7,18-bis(2-methoxycarbonylethyl)-8,17-dimethylpyreno[4,5-b]porphyrinatocopper(II) (**28b**).* A saturated solution of copper(II) acetate in methanol (3 mL) was added to a solution pyrenoporphyrin **15b** (10.0 mg, 0.0135 mmol) in chloroform (10 mL) and the resulting mixture heated under reflux for 1 h. The mixture was cooled, washed with water and the solvent evaporated under reduced pressure. Recrystallization from chloroform–methanol gave the copper(II) complex (8.4 mg, 0.010 mmol, 77%) as green crystals, mp 257–258 °C, dec; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 422 (5.07), 543 (3.83), 588 nm (4.34). HRMS (FAB), m/z calcd for $C_{48}H_{42}CuN_4O_4$+H: 802.2580. Found: 802.2579.

*4.2.15. 12,13-Diethyl-7,18-bis(2-methoxycarbonylethyl)-8,17-dimethylpyreno[4,5-b]porphyrinatozinc(II) (**28c**).* Pyrenoporphyrin **15b** (10.0 mg, 0.0135 mmol) and zinc acetate (6 mg) were refluxed with DMF (10 mL) for 1 h. The mixture was diluted with chloroform, washed with water and evaporated under reduced pressure. Recrystallization from chloroform–methanol gave the zinc chelate (10.8 mg, quantitative) as a green powder (chloroform–methanol), mp >300 °C; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 428 (5.01), 553 (3.93), 595 nm (4.33); UV–vis (1% pyrrolidine–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 444 (5.14), 562 (4.03), 603 (4.35), 672 nm (3.65); ^{1}H NMR (400 MHz, pyrrolidine–$CDCl_3$): δ 1.91 (6H, t, J=7.6 Hz), 3.40 (4H, t, J=7.8 Hz), 3.67 (6H, s), 3.68 (6H, s), 4.07 (4H, q, J=7.6 Hz), 4.58 (4H, t, J=7.6 Hz), 8.28 (2H, s), 8.43 (2H, d, J=7.6 Hz), 8.54 (2H, t, J=7.6 Hz), 10.01 (2H, s), 10.54 (2H, d, J=7.6 Hz), 11.27 (2H, s); ^{13}C NMR (pyrrolidine–$CDCl_3$): δ 12.0, 18.8, 19.9, 22.7, 37.9, 51.9, 97.5, 100.1, 123.9, 125.4, 127.0, 127.2, 128.2, 129.3, 132.6, 134.5, 136.9, 139.3, 142.6, 145.0, 147.5, 148.7, 148.8, 173.9. HRMS (FAB), m/z calcd for $C_{48}H_{42}N_4O_4Zn$+H: 803.2579. Found: 803.2576.

*4.2.16. 7,18-Bis(2-isobutoxycarbonylethyl)-8,17-dimethyldipyreno[4,5-b:4,5-l]porphyrin (**32b**).* Nitrogen gas was bubbled through a pear shaped flask containing tripyrrane **26b** (150 mg, 0.188 mmol) and TFA (2 mL) for 10 min. Dichloromethane (38 mL) was added, followed immediately by pyrenopyrrole dialdehyde **29** (54 mg; 0.18 mmol), and the reaction mixture stirred under nitrogen in the dark for 3 h. The reaction mixture was washed with water and the combined organic layers shaken vigorously with 0.1% w/v aqueous ferric chloride solution for 20 min. The solution was then washed with water, sodium bicarbonate solution and water, and evaporated under reduced pressure. The residue was dissolved in a mixture of 2-methyl-1-propanol (50 mL) and concd sulfuric acid (2.5 mL), and refluxed for 4 h under nitrogen to bring about transesterification of the propionate side chains. The solution was diluted with chloroform, and washed with water, sodium bicarbonate solution and water, and evaporated under reduced pressure. The residue was recrystallized from chloroform–methanol to give the *opp*-dipyrenoporphyrin (74 mg, 0.079 mmol, 44%) as green crystals, mp 269–270 °C, dec; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 428 (5.27), 578 (4.64), 594 nm (4.47); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 436 (5.07), 453 (5.09), 593 (4.39), 643 nm (4.50); ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.0 (2H, br s), 0.73 (12H, d, J=7.0 Hz), 1.77 (2H, m), 3.00 (4H, br t), 3.30 (6H, br s), 3.83 (4H, d, J=6.4 Hz), 4.11 (4H, br t), 8.37–8.38 (4H, overlapping doublets), 7.90–8.55 (10H, m), 8.42–8.52 (6H, m), 9.95 (1H, br s), 10.09 (1H, br s), 10.41 (1H, br s), 10.54 (1H, br s); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): δ −2.2 (2H, br s), −0.78 (2H, br s), 0.89 (12H, d, J=7.2 Hz), 1.94 (2H, nonet, J=6.6 Hz), 3.25 (4H, t, J=7.2 Hz), 3.70 (6H, s), 4.02 (4H, d, J=6.4 Hz), 4.42 (4H, t, J=7.2 Hz), 8.38 (2H, s), 8.39 (2H, s), 8.64–8.73 (6H, m), 10.19 (2H, dd, J=2.4, 6.4 Hz), 10.41 (2H, d, J=7.6 Hz), 11.47 (2H, s), 11.76 (2H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 12.4, 19.2, 21.9, 27.9, 35.7, 71.7, 100.3, 100.6, 125.0, 125.6, 126.7, 126.8, 127.1, 127.2, 128.0, 128.1, 128.6 (2), 128.7, 130.4, 130.7, 132.7, 132.8, 138.0, 138.9, 139.4, 139.8, 143.5, 143.7, 173.5. HRMS (FAB), m/z calcd for $C_{64}H_{54}N_4O_4$+H: 943.4225. Found: 943.4223. Anal. Calcd for $C_{64}H_{54}N_4O_4\cdot{}^1/_8CHCl_3$: C, 80.39; H, 5.69; N, 5.85. Found: C, 80.35; H, 5.54; N, 5.96.

*4.2.17. [7,18-Bis(2-isobutoxycarbonylethyl)-8,17-dimethyldipyreno[4,5-b:4,5-l]porphyrinato]nickel(II) (**33a**).* Dark green crystals, mp 250 °C, dec (chloroform–methanol); UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 434 (4.82), 609 nm (4.42); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69 (12H, t, J=6.8 Hz), 1.70–1.76 (2H, m), 2.90 (4H, br t), 3.36 (6H, s), 3.79 (4H, d, J=6.8 Hz), 4.17 (4H, br t), 8.08 (4H, d, J=7.6 Hz), 8.19–8.23 (8H, m), 9.33 (2H, br d), 9.37 (2H, br d), 9.79 (2H, s), 9.81 (2H, s). HRMS (FAB), m/z calcd for $C_{64}H_{52}N_4NiO_4$: 998.3341. Found: 998.3342.

*4.2.18. [7,18-Bis(2-isobutoxycarbonylethyl)-8,17-dimethyldipyreno[4,5-b:4,5-l]porphyrinato]copper(II) (**33b**).* Dark green crystals, mp >300 °C (chloroform–methanol); UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 434 (4.60), 615 nm (4.09). HRMS (FAB), m/z calcd for $C_{64}H_{52}CuN_4O_4$: 1003.3285. Found: 1003.3285.

*4.2.19. [7,18-Bis(2-isobutoxycarbonylethyl)-8,17-dimethyldipyreno[4,5-b:4,5-l]porphyrinato]zinc(II) (**33c**).* Dark green crystals, mp >300 °C (chloroform–methanol); UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 454 (5.12), 576 (3.78), 626 nm (4.31); UV–vis (1% pyrrolidine–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 455 (5.14), 577 (3.87), 628 nm (4.51); ^{1}H NMR (400 MHz, pyrrolidine–$CDCl_3$; downfield region only): δ 8.20 (2H, s), 8.26 (2H, s), 8.35 (2H, d, J=7.2 Hz), 8.41 (4H, d, J=7.2 Hz), 8.49 (2H, t, J=7.2 Hz), 10.27 (2H, d, J=7.6 Hz), 10.40 (2H, d, J=8 Hz), 10.99 (2H, s), 11.05 (2H, s). HRMS (FAB), m/z calcd for $C_{64}H_{52}N_4O_4Zn$: 1004.3280. Found: 1004.3277.

*4.2.20. 13,17-Bis(2-isobutoxycarbonylethyl)-12,18-dimethyldipyreno[4,5-b:4,5-g]porphyrin (**39b**).* Diethyl 1,1′-dipyreno[4,5-*c*]pyrrolylmethane-3,3′-dicarboxylate (**36**; 150 mg, 0.235 mmol) and potassium hydroxide (205 mg) were dissolved in ethylene glycol (21 mL). Nitrogen was allowed to bubble through the mixture for 5–10 min before placing the reaction flask in a preheated oil bath (190–200 °C). The mixture was heated under reflux under an atmosphere of nitrogen for 30 min. The reaction mixture was cooled and diluted with chloroform, washed with water, and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue taken up in 280 mL of dichloromethane and 13 mL of methanol. Dialdehyde **37** (85 mg, 0.21 mmol) was added, followed by a solution of *p*-toluenesulfonic acid (406 mg) in methanol (13 mL), and the solution was stirred in the dark at room temperature overnight. A saturated solution of zinc acetate in methanol (7 mL) was added to the mixture and stirring was continued for an additional two days. The mixture was washed with water, dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in a mixture of sulfuric acid (2.5 mL) and 2-methyl-1-propanol and the solution was refluxed under nitrogen for 4 h. The mixture was cooled to room temperature, diluted with dichloromethane and washed sequentially with water, saturated sodium bicarbonate solution, and water. The solvent was evaporated under reduced pressure and the residue was recrystallized three times with chloroform–methanol to give the *adj*-dipyrenoporphyrin (106 mg, 0.112 mmol, 53%) as dark purple crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max}

($\log_{10}\varepsilon$) 387 (4.57), 440 (5.10), 537 (4.29), 574 (4.41), 596 (4.16), 655 nm (4.15); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 449 (5.18), 589 (4.40), 637 nm (4.36); UV–vis (5% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 402 (sh, 4.59), 449 (5.12), 532 (4.43), 592 (4.40), 638 nm (4.33); ^{1}H NMR (400 MHz, $CDCl_3$): δ −5.75 (2H, br s), 0.90 (12H, d, J=6.8 Hz), 1.92 (2H, nonet, J=6.7 Hz), 2.77 (6H, s), 2.94 (4H, t, J=7.6 Hz), 3.76 (4H, t, J=8.0 Hz), 4.16 (4H, d, J=6.8 Hz), 7.41 (2H, t, J=7.6 Hz), 7.85 (2H, d, J=7.6 Hz), 7.94 (2H, d, J=8.0 Hz), 8.01–8.06 (4H, m), 8.14–8.18 (4H, m), 9.04 (1H, s), 9.12 (2H, d, J=7.6 Hz), 9.25 (1H, br s), 9.45 (2H, s); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): δ −2.18 (2H, br s), −1.74 (2H, br s), 0.91 (12H, d, J=6.8 Hz), 1.94 (2H, nonet, J=6.6 Hz), 3.15 (4H, t, J=8.0 Hz), 3.74 (6H, s), 3.96 (4H, d, J=6.4 Hz), 4.46 (4H, t, J=8.0 Hz), 8.45 (4H, s), 8.65 (2H, t, J=7.6 Hz), 8.68–8.74 (6H, m), 10.09 (2H, d, J=7.0 Hz), 10.26 (2H, dd, J=3.0, 6.0 Hz), 10.82 (1H, s), 11.58 (2H, s), 12.66 (1H, s); ^{13}C NMR ($CDCl_3$): δ 12.3, 19.0, 21.9, 27.8, 35.8, 72.2, 98.9, 100.5, 102.5, 125.0, 125.4, 126.7, 126.8, 127.3, 127.5, 128.2, 128.3, 128.7, 128.9, 129.0, 130.2, 131.0, 133.0, 138.8, 139.4, 139.7, 140.3, 143.1, 143.4, 174.5. HRMS (FAB), m/z calcd for $C_{64}H_{54}N_4O_4$+H: 943.4225. Found: 943.4223.

*4.2.21. [13,17-Bis(2-isobutoxycarbonylethyl)-12,18-dimethyldipyrreno[4,5-b:4,5-g]porphyrinato]nickel(II) (**40a**).* Dark green crystals, mp >300 °C (chloroform–methanol); UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 436 (4.88), 556 (4.02), 599 nm (4.40); ^{1}H NMR ($CDCl_3$): δ 0.80 (12H, d, J=6.0 Hz), 1.77–1.85 (2H, br m), 2.46 (6H, s), 2.82 (4H, br t), 3.75 (4H, br t), 3.85 (4H, d, J=6.0 Hz), 7.96–8.04 (2H, br), 8.10–8.25 (8H, m), 8.30–8.40 (4H, m), 8.62–8.72 (2H, br), 8.78–8.86 (2H, br), 8.88 (1H, br s), 9.72 (1H, br s). HRMS (FAB), m/z calcd for $C_{64}H_{52}N_4NiO_4$: 998.3342. Found: 998.3341.

*4.2.22. [13,17-Bis(2-isobutoxycarbonylethyl)-12,18-dimethyldipyrreno[4,5-b:4,5-g]porphyrinato]copper(II) (**40b**).* Dark green crystals, mp >300 °C (chloroform–methanol); UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 438 (4.93), 562 (4.08), 605 nm (4.38). HRMS (FAB), m/z calcd for $C_{64}H_{52}CuN_4O_4$: 1003.3285. Found: 1003.3285.

*4.2.23. [13,17-Bis(2-isobutoxycarbonylethyl)-12,18-dimethyldipyrreno[4,5-b:4,5-g]porphyrinato]zinc(II) (**40c**).* Dark green crystals, mp >300 °C; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 446 (5.18), 572 (4.40), 613 nm (4.66); UV–vis (1% pyrrolidine–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 461 (5.12), 578 (4.27), 619 nm (4.49); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (12H, d, J=6.4 Hz), 1.88–1.96 (2H, m), 2.23 (6H, br s), 2.70 (4H, br t), 3.30 (4H, br t), 3.93 (4H, d, J=6.8 Hz), 6.44–6.60 (2H, br), 6.96–7.05 (2H, br), 7.44–7.60 (6H, br), 7.62–7.68 (2H, br), 7.8–8.2 (5H, v br), 8.50–8.60 (2H, br), 8.64–8.72 (1H, br); ^{1}H NMR (400 MHz, one drop pyrrolidine–$CDCl_3$): δ 0.90 (12H, t, J=6.4 Hz), 1.79 (2H, nonet), 3.34 (4H, t, J=7.8 Hz), 3.65 (6H, s), 3.99 (4H, d, J=6.8 Hz), 4.38 (4H, t, J=7.8 Hz), 8.18–8.23 (6H, m), 8.25 (2H, t, J=7.8 Hz), 8.34–8.42 (4H, 2 overlapping triplets), 9.85 (1H, s), 9.98 (2H, d, J=7.2 Hz), 10.20 (2H, d, J=7.2 Hz), 10.90 (2H, s), 11.78 (1H, s). HRMS (FAB), m/z calcd for $C_{64}H_{52}N_4O_4Zn$: 1004.3280. Found: 1004.3277.

*4.2.24. 7,18-Dibutyl-8,17-dimethylphenanthrolino[9,10-b]pyreno[4,5-l]porphyrin (**35**).* Nitrogen gas was gently bubbled through a pear shaped flask containing tripyrrane **34** (100 mg, 0.139 mmol) and TFA (2 mL) for 10 min. Dichloromethane (38 mL) was added, followed immediately by pyrenopyrrole dialdehyde **29** (42 mg, 0.14 mmol), and the reaction mixture stirred under nitrogen in dark for 3 h. The mixture was neutralized by the dropwise addition of Et_3N, DDQ (33 mg) was added, and stirring was continued for an additional 1 h. The solution was then diluted with chloroform, washed with water and the solvent evaporated under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with chloroform. Recrystallization from chloroform–methanol gave the porphyrin (54 mg, 0.070 mmol, 50%) as a dark green powder, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 431 (4.89), 580 (4.29), 604 nm (4.25); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 444 (5.05), 529 (4.02), 577 (4.03), 600 (4.08), 654 nm (4.55); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): δ −2.00 (1H, br s), −0.77 (3H, br s), 1.00 (6H, t, J=7.6 Hz), 1.53–1.62 (4H, m), 1.97–2.06 (4H, m), 3.68 (6H, s), 4.13 (4H, t, J=7.4 Hz), 8.45 (2H, s), 8.70–8.75 (6H, m), 9.66 (2H, d, J=4.8 Hz), 10.18 (2H, dd, J=1.2, 6.4 Hz), 10.57 (2H, d, J=8.4 Hz), 11.18 (2H, s), 11.48 (2H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 12.4, 13.9, 23.1, 26.9, 34.3, 100.0, 100.4, 124.9, 125.0, 126.3, 126.9, 127.3, 127.8, 128.3, 128.8, 129.4, 131.3, 132.9, 135.6, 138.0, 139.9, 140.2, 141.3, 143.3, 144.0, 146.5, 147.9. HRMS (FAB), m/z calcd for $C_{54}H_{44}N_6$+H: 777.3706. Found: 777.3706.

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Supplementary data

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References and notes

1. (a) Kim, D.; Osuka, A. *Acc. Chem. Res.* **2004**, *37*, 735; (b) Boyd, P. D. W.; Reed, C. A. *Acc. Chem. Res.* **2005**, *38*, 235; (c) Balaban, T. S. *Acc. Chem. Res.* **2005**, *38*, 612.
2. (a) Ostovic, D.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314; (b) Dolphin, D.; Traylor, T. G.; Xie, L. Y. *Acc. Chem. Res.* **1997**, *30*, 251; (c) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411; (d) Aida, T.; Inoue, S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 6, pp 133–156.
3. Hwang, I.-W.; Cho, H. S.; Jeong, D. H.; Kim, D.; Tsuda, A.; Nakamura, T.; Osuka, A. *J. Phys. Chem. B* **2003**, *107*, 9977.
4. Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469.
5. (a) Nakash, M.; Sanders, J. K. M. *J. Org. Chem.* **2000**, *65*, 7266; (b) Ikeda, A.; Ayabe, M.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *Org. Lett.* **2000**, *2*, 3707.
6. Anderson, H. L. *Chem. Commun.* **1999**, 2323; Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759; Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed.* **1997**, *36*, 135; Winters, M. U.; Dahlstedt, E.; Blades, H. E.; Wilson, C. J.; Frampton, M. J.; Anderson, H. L.; Albinsson, B. *J. Am. Chem. Soc.* **2007**, *129*, 4291; Ozawa, H.; Kawao, M.; Tanaka, H.; Ogawa, T. *Langmuir* **2007**, *23*, 6365.
7. Balakumar, A.; Lysenko, A. B.; Carcel, C.; Malinovskii, V. L.; Gryko, D. T.; Schweikart, K.-H.; Loewe, R. S.; Yasseri, A. A.; Liu, Z.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 1435.
8. (a) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1987**, 39; (b) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569.
9. (a) Reimers, J. R.; Hall, L. E.; Crossley, M. J.; Hush, N. S. *J. Phys. Chem. A* **1999**, *103*, 4385; (b) Sendt, K.; Johnston, L. A.; Hough, W. A.; Crossley, M. J.; Hush, N. S.; Reimers, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 9299; (c) Kadish, K. M.; Wenbo, E.; Sintic, P. J.; Ou, Z.; Shao, J.; Ohkubo, K.; Fukuzumi, S.; Govenlock, L. J.; McDonald, J. A.; Try, A. C.; Cai, Z.-L.; Reimers, J. R.; Crossley, M. J. *J. Phys. Chem. B* **2007**, *111*, 8762.
10. Uno, H.; Masumoto, A.; Ono, N. *J. Am. Chem. Soc.* **2003**, *125*, 12082.
11. Jaquinod, L.; Siri, O.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1261.
12. Vicente, M. G. H.; Cancilla, M. T.; Lebrilla, C. B.; Smith, K. M. *Chem. Commun.* **1998**, 2355.
13. Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79.
14. Nakamura, Y.; Aratani, N.; Shinokubo, H.; Takagi, A.; Kawai, T.; Matsumoto, T.; Yoon, Z. S.; Kim, D. Y.; Ahn, T. K.; Kim, D.; Muranaka, A.; Kobayashi, N.; Osuka, A. *J. Am. Chem. Soc.* **2006**, *128*, 4119.
15. (a) Lash, T. D.; Denny, C. P. *Tetrahedron* **1995**, *51*, 59; (b) Lash, T. D.; Roper, T. J. *Tetrahedron Lett.* **1994**, *35*, 7715; (c) Manley, J. M.; Roper, T. J.; Lash, T. D. *J. Org. Chem.* **2005**, *70*, 874.
16. Lash, T. D.; Gandhi, V. *J. Org. Chem.* **2000**, *65*, 8020.
17. (a) Lash, T. D.; Novak, B. H. *Tetrahedron Lett.* **1995**, *36*, 4381; (b) Lash, T. D.; Novak, B. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 683; (c) Novak, B. H.; Lash, T. D. *J. Org. Chem.* **1998**, *63*, 3998.
18. (a) Lin, Y.; Lash, T. D. *Tetrahedron Lett.* **1995**, *36*, 9441; (b) Lash, T. D.; Lin, Y.; Novak, B. H.; Parikh, M. D. *Tetrahedron* **2005**, *61*, 11601.
19. (a) Lash, T. D.; Wijesinghe, C.; Osuma, A. T.; Patel, J. R. *Tetrahedron Lett.* **1997**, *38*, 2031; (b) Chandrasekar, P.; Lash, T. D. *Tetrahedron Lett.* **1996**, *37*, 4873; (c) Lash, T. D.; Chandrasekar, P.; Osuma, A. T.; Chaney, S. T.; Spence, J. D. *J. Org. Chem.* **1998**, *63*, 8455.
20. (a) Lash, T. D.; Chandrasekar, P. *J. Am. Chem. Soc.* **1996**, *118*, 8767; (b) Spence, J. D.; Lash, T. D. *J. Org. Chem.* **2000**, *65*, 1530.
21. Lash, T. D.; Werner, T. M.; Thompson, M. L.; Manley, J. M. *J. Org. Chem.* **2001**, *66*, 3152.

22. Cillo, C. M.; Lash, T. D. *Tetrahedron* **2005**, *61*, 11615.
23. Lash, T. D.; Novak, B. H.; Lin, Y. *Tetrahedron Lett.* **1994**, *35*, 2493.
24. Lash, T. D. *Chem.—Eur. J.* **1996**, *2*, 1197.
25. (a) Barton, D. H. R.; Kervagoret, J.; Zard, S. Z. *Tetrahedron* **1990**, *46*, 7587; (b) Ono, N.; Kawamura, H.; Bougauchi, M.; Maruyama, K. *Tetrahedron* **1990**, *46*, 7483; (c) Lash, T. D.; Bellettini, J. R.; Bastian, J. A.; Couch, K. B. *Synthesis* **1994**, 170.
26. Gribble, G. W. In *"Barton–Zard Reaction" in Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, 2005; pp 70–78.
27. Ono, N.; Hironaga, H.; Ono, K.; Kaneko, S.; Murashima, T.; Ueda, T.; Tsukamura, C.; Ogawa, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 417.
28. Bag, N.; Chern, S.-S.; Peng, S.-M.; Chang, C. K. *Tetrahedron Lett.* **1995**, *36*, 6409.
29. Lash, T. D.; Thompson, M. L.; Werner, T. M.; Spence, J. D. *Synlett* **2000**, 213.
30. Lash, T.D.; Gandhi, V. Book of Abstracts, Preliminary results from these studies were presented at the 221st National Meeting of the American Chemical Society, San Diego, CA, April 2001, ORGN 713.
31. Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 2, pp 125–199.
32. (a) Bavin, P. M. G.; Dewar, M. J. S. *J. Chem. Soc.* **1956**, 164; (b) Paputa-Peck, M. C.; Marano, R. S.; Schuetzle, D.; Riley, T. L.; Hampton, C. V.; Prater, T. J.; Skewew, L. M.; Jensen, T. E.; Ruehle, P. H.; Bosch, L. C.; Duncan, W. P. *Anal. Chem.* **1983**, *55*, 1946.
33. (a) Lund, H.; Berg, A. *Kgl. Danske Videnskab. Selskab., Mat. fys. Medd.* **1946**, *22*, 17; (b) Berg, A.; Jakobsen, H. J.; Johansen, S. R. *Acta Chem. Scand.* **1969**, *23*, 567; (c) Yamato, T.; Miyazawa, A.; Tashiro, M. *Chem. Ber.* **1993**, *126*, 2505.
34. Rodenburg, L.; Brandsma, R.; Tintel, C.; van Thuijl, J.; Lugtenburg, J.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 156.
35. However, Friedel–Craft acylation of 2,7-di-*tert*-butylpyrene does occur at the 4-position.[33c]
36. van den Braken-van Leersum, A. M.; Tintel, C.; van't Zelfde, M.; Cornelisse, J.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 120.
37. (a) Cook, J. W.; Hewett, C. L. *J. Chem. Soc.* **1933**, 398; (b) Hansen, P. E.; Blaabjerg, O.; Berg, A. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 720.
38. Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973.
39. Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921.
40. For a recent report on the synthesis of ruthenium(II) complexes of phenanthrolinoporphyrins, see: Okujima, T.; Mifuji, A.; Nakamura, J.; Yamada, H.; Uno, H.; Ono, N. *Org. Lett.* **2009**, *11*, 4088–4091.
41. Cavaleiro, J. A. S.; Rocha Gonsalves, A. M. d'A.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1771.
42. (a) Lash, T. D. *Tetrahedron* **1998**, *54*, 359; (b) Shiner, C. M.; Lash, T. D. *Tetrahedron* **2005**, *61*, 11628.
43. Lash, T. D. *J. Porphyrins Phthalocyanines* **2001**, *5*, 267.
44. Medforth, C. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 5, pp 1–80.
45. Lash, T. D. *J. Porphyrins Phthalocyanines* **1997**, *1*, 29.
46. Clezy, P. S.; Liepa, A. J. *Aust. J. Chem.* **1970**, *23*, 2443.
47. Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1979**, *59*, 183.
48. Tardieux, C.; Bolze, F.; Gros, C. P.; Guilard, R. *Synthesis* **1998**, 267.
49. Clezy, P. S.; Fookes, C. J. R.; Liepa, A. J. *Aust. J. Chem.* **1972**, *25*, 1979.