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The design and synthesis of porphyrin/oligiothiophene hybrid monomers

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In an effort to build effective photovoltaic cells based on porphyrin-functionalised polythiophenes we have focused on synthetic routes to three monomer types. By controlling the geometric structure of the monomer, oxidation of these materials should produce polymers with different architectural structures, and as a result, different opto-electronic properties. Employing Wittig protocols allowed access to monomers in which the porphyrin moiety is connected to the β-position of the thiophene *via* an alkene linkage. In addition, monomers were constructed using porphyrin condensation methods to afford α-thiophene *meso*-substituted porphryins. Another set of monomers was also prepared *via* porphyrin condensation routes, but instead utilising β-formylthiophenes. By utilising different formyloligothiophenes we were able to generate a series of monomers that can be used to control the loading of the porphyrin in the polythiophene matrix.

Introduction

Since their discovery, Inherently Conducting Polymers (ICPs) have held a special place in material science. The ability to design organic polymers that exhibit desirable electronic and opto-electronic properties has resulted in an explosion of applications, *e.g.* LEDs, electrochromics, photovoltaics, electrocatalysis and sensor devices.[1] In particular, these polymers have been used to develop hybrid materials that, when combined, optimise the properties of the individual components or, ideally, have properties that outweigh the sum of the parts – *i.e.* "synergic materials".[2]

In recent years, significant interest has focused on using hybrid materials in photovoltaic devices as an alternative to silicon-based technology. One approach has been to use an organic component, such as a dye, and an inorganic component, such as a conductive metal-based film. To date, the most commercially advanced hybrid photocell device of this type is the Gratzel ruthenium-bipyridyl/TiO_2/liquid electrolyte cell.[3] However, there is still a need to minimise fabrication costs, reduce construction complexity and to increase photoenergy conversion in photocells. In theory, this can be achieved by optimising the key components of a photocell, such as the characteristics of the metal oxide surface, the effectiveness of the light-capturing system and the charge separation/transportation processes.[4] One such area of interest has been solid-state solar cells designed from conducting polythiophenes that incorporate light-harvesting systems. For instance, photocurrents have been obtained from polymers derived from oligothiophenes axially coordinated to phosphorous-centred porphyrins,[5] from fullerenes grafted onto the backbone of polythiophene[6] and, more recently, from ordered polythiophenes that contain simple organic donor and/or acceptor groups,[7] or from mixed porphyrin–acetylene–thiophene copolymers.[8]

Our group has previously been concerned with the synthesis and study of porphyrins as artificial light harvesters,[9] and, more recently, in making new functionalised conducting polymers from terthiophene monomers.[10] Combining these two areas of research, we were intrigued as to how the opto-electronic properties of the photocell could be improved by manipulating the molecular architecture of the porphyrin/thiophene polymer deposited on the metal oxide surface. Structural order at a molecular level, in part, can be imprinted by the design of the monomeric unit.[11] A number of approaches can be taken to this, as shown by Fig. 1. Types I–III are similar in that the porphyrin unit is covalently attached to the β-position of the polymer backbone. Type I polymers, where the porphyrin is attached to the thiophene backbone *via* an alkyl linker, have been synthesised and studied for electrocatalysis and for use in sensor devices.[12] However, in these hybrid systems, the polymer

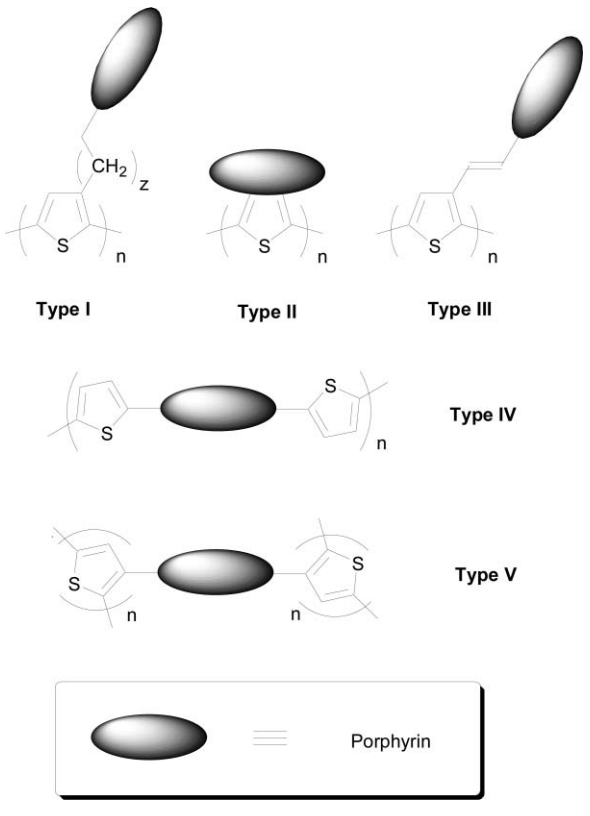

Fig. 1 Graphical representation of Type I–V polymer structures.

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primarily acts as a platform and the redox properties of the porphyrin are essentially the same as the untethered macrocycle. Alternatively, the porphyrin can be attached to the polymer chain by fusion to the C-side of thiophene (Type II) or *via* a conjugated linker (Type III). Materials of this type may have interesting electronic properties, as electronic communication between the two moieties should be possible. Type II thiophene monomers have been successfully synthesised to study self-assembly onto gold surfaces.[13] Unfortunately, it is yet to be seen if polymerisation of these porphyrin-fused thiophene materials will provide conducting polymers with desirable electronic properties. We have recently developed an efficient method to rapidly construct a variety of functionalised terthiophene monomers that form electro-active films of Type III structure.[10] Type IV and V monomers are common in that the methodology used to synthesise *meso*-aryl-substituted porphyrins has been applied in this approach. Interestingly, porphyrin monomers synthesised from 2-substituted thiophenes could provide linear or lattice type polymers (Type IV) where the porphyrin lies embedded in the polymer chain. Alternatively, 3-subsituted thiophenes may afford ladder or column structures (Type V) where the porphyrin acts as a cross-linker connecting polymer strands. This paper will discuss our efforts towards the development of practical synthetic routes to porphyrin/oligothiophene monomeric materials of the Type III, IV and V.

Results and discussion

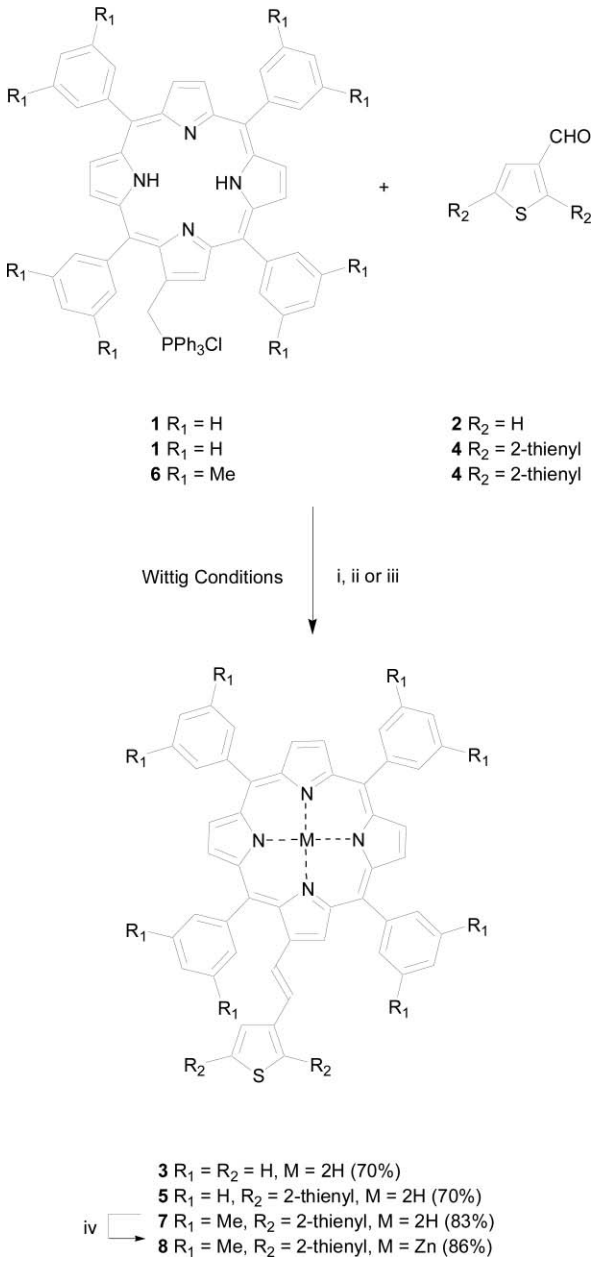
1. Synthesis and characterisation of Type III monomers

Thiophene monomers of Type III structure were constructed utilising the Wittig methodology developed by our group to build porphyrin arrays[9] and functionalised terthiophene monomers.[10] The simplest of these structures is the 3-substituted thiophene derivative **3** (Scheme 1).

Reaction of the 5,10,15,20-tetraphenylporphyrin phosphonium salt (TPPps) **1** and commercially available 3-formylthiophene **2** with triethylamine at ambient temperature gave a mixture of geometric isomers, as determined by ^{1}H NMR spectroscopy. Analysis of this mixture by TLC indicated the isomers could not be separated and, therefore, isomerisation to the all-*trans* product was accomplished by subjecting the crude mixture to a solution of iodine in dichloromethane. Thus TPP-thiophene **3** was obtained after chromatography and recrystallisation as a purple–brown solid in good yield (70%). The ^{1}H NMR spectrum of **3** has signals that are consistent with the construction of the double bond between the porphyrin and thiophene ring. The alkene protons appear as two doublets at 6.76 and 7.32 ppm, with a large coupling constant (J = 16.2 Hz) consistent with a *trans* geometry. The AMX spin system of the thiophene protons was identified as a set of multiplets occurring between 6.9–7.3 ppm. As expected, the β-pyrrolic and porphyrin aromatic protons are located further downfield in the 7.6–9.0 ppm region, and the amine protons are observed in the upfield region at −2.61 ppm.

Since previous studies directed at the electrochemical oxidation of β-substituted styrylthiophenes have indicated that these simple monomers do not necessarily form satisfactory homopolymers,[7a,14] we chose to also synthesise the TPP-terthiophene homologue. The synthesis of this material should allow us to control the loading levels of porphyrin between homopolymers **3** and **5** and thus determine how it influences photocell efficiency. The conditions described in the synthesis of **3** were employed to prepare **5**. Reaction of the building block 3′-formyl-2,2′:5′,2″-terthiophene **4** with TPPps **1** under Wittig conditions afforded an inseparable mixture of *cis* and *trans* isomers. Attempts to transform the *cis* to the *trans* isomer using elemental iodine were unsuccessful, giving complex mixtures as indicated by TLC and NMR. Instead, it was found that the all-*trans* product **5** could be generated directly, and in satisfactory yield (70%), by performing the Wittig reaction at an elevated temperature by irradiation with a tungsten lamp source. Analysis of the ^{1}H NMR spectrum of **5** proved very difficult, as the majority of β-pyrrolic, phenyl and thiophene signals resonate in the region 6.9–8.1 ppm. However, the *trans* double bond is evident as two doublets (6.81 and 7.66 ppm) with a large coupling constant (J = 16.0 Hz), while a broad singlet at −2.62 ppm for the secondary amine protons is clearly distinguishable. Full assignment of this compound was achieved from coupling constants, the long range COSY[10c] spectrum and with the aid of data obtained from the TXP-terthiophene compound **7** (see below). During purification and characterisation, it was observed that **5** had limited solubility in a number of organic solvents, and this was considered to be problematic for electrochemical studies. As a consequence, a more soluble precursor based on octamethyl-substituted porphyrin, 5,10,15,20-tetra(xylyl)porphyrin (TXP), was prepared.

In comparison to the synthesis of compounds **3** and **5**, formation of TXP-terthiophene **7** and the zinc-metallated **8**



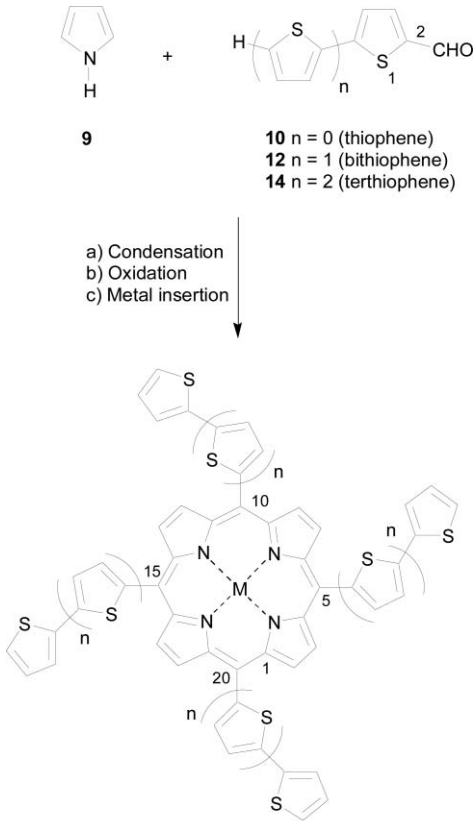
Scheme 1 Synthesis of Type III porphyrin/thiophene monomers. *Reagents and conditions*: Compound **3**, i) DCM, NEt_3, RT, then I_2, DCM, dark, RT; Compound **5**, ii) $ClCH_2CH_2Cl$, DBU, light; Compound **7**, iii) PhMe, DBU, heat; Compound **8**, iv) $Zn(OAc)_2{\cdot}2H_2O$, MeOH, $CHCl_3$, RT.

were facile. Reaction of 3′-formyl-2,2′:5′,2″-terthiophene **4** with TXP phosphonium salt (TXPps) **6** was best achieved by heating in toluene using DBU as base. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated that only the *trans* isomer was present. Column chromatography of this crude material afforded the TXP analogue **7** as a purple solid in high yield (83%) and, as predicted, with better solubility properties than TPP-terthiophene **5**. The ^{1}H NMR spectrum of the TXP-terthiophene **7** is less complex due to the presence of the methyl groups on the phenyl rings which dramatically reduces the congestion of signals in the aromatic region. Interestingly, even though **7** lacks symmetry, the methyl groups attached to the phenyl rings appear as two singlets, at 2.59 and 2.61 ppm, which integrate for 18 and 6 protons respectively. Using ^{1}H NMR spectrum and 2D NMR experiments, compound **7** was easily assigned. This information was helpful for assigning the more complex spectrum of **5**.

2. Synthesis and characterisation of Type IV monomers

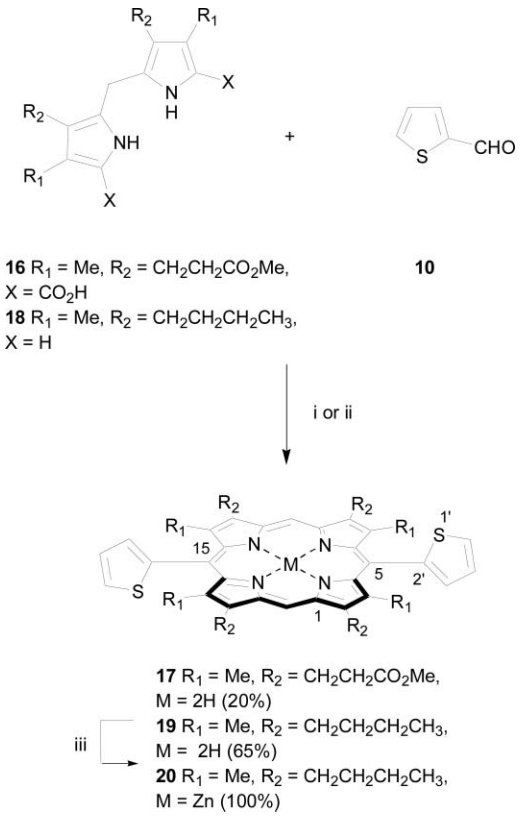
Since the first reported synthesis of *meso*-tetraarylporphyrins, a number of modifications and alternative syntheses have been developed to access tetra- and di-aryl *meso*-substituted porphyrins.[15]

2.1 Tetra(α-oligothienyl) *meso*-substituted porphyrins. A search of the literature for the simplest of the possible known 5,10,15,20-oligothiophenes indicated that substituted 2-thienyl, or α-thiophene, free-base and metalloporphyrins have been synthesised for potentially useful magnetic and redox properties.[16] Using classical porphryin condensation protocols,[17] reaction of 2-formylthiophene **10** with pyrrole **9** in the presence of an acid catalyst afforded the porphyrinogen, which was subsequently oxidised to the free-base porphyrin **11** (Scheme 2). Insertion of a metal ion into the porphyrin macrocycle is readily achieved by using the acetate method.[18] However, prior to our research Shimadzu and colleagues had envisaged the use of *meso*-substituted oligothiophene porphyrins as suitable precursors to "molecular wires". Thus the thiophene **11**, bithiophene **13** and terthiophene **15** porphyrin derivatives were synthesised (Scheme 2), polymerised and tested in photovoltaic devices.[5] Although quantitative photocurrent values were not provided for any of the polymers studied, interesting results were reported. Electrochemical oxidation of thiophene monomer **11** did not produce homopolymers, while monomers **13** and **15** easily formed desirable polymeric materials. More encouragingly, both poly-**13** and poly-**15**, when incorporated into Schotty devices, were shown to produce photocurrents upon irradiation with white light.[5b,c]



Scheme 2 Synthesis of tetra(α-oligothienyl) *meso*-substituted porphyrins.

2.2 5,15-Bis(α-thiophene)porphyrins. In contrast to the tetrasubstituted α-thiophene derivatives described previously, a review of the literature revealed only one report of a 5,10-disubstituted (α-thiophene)porphyrin. Using MacDonald condensation protocols,[19] reaction of dipyrrylmethanedicarboxylic acid **16** and 2-formylthiophene **10** in the presence of acid catalyst, followed by the necessary oxidative step, gave 5,15-bis(α-thiophene)porphyrin **17** as a purple solid in 20% yield (Scheme 3).[20] Given the low yield of **17** and the limited stability of the ester functionality to electrochemical conditions, we chose to find a derivative that was better suited to our requirements. Using Lindsey conditions,[17b] the alkylated dipyrrylmethane derivative **18** was reacted with aldehyde **10** in the presence of catalytic *p*-toluenesulfonic acid to afford a porphyrinogen intermediate. This material was not isolated, but subjected to oxidative conditions with *p*-chloroanil to give the target porphyrin **19** as a dark purple powder in high yield (65%). Treatment of this free base material **19** under standard acetate



Scheme 3 Synthesis of Type IV 5,15-bis(α-thiophene)porphyrin monomers. *Reagents and conditions*: Compound **17**, i) EtOH, trichloroacetic acid, RT, then THF, DDQ; Compound **19**, ii) *p*-TsOH·H_2O, MeOH, RT; then DCM, *p*-chloranil; Compound **20**, iii) $Zn(OAc)_2$·$2H_2O$, MeOH, $CHCl_3$, RT.

conditions resulted in smooth conversion to the zinc species **20** in quantitative yield. Both these thiophene-appended porphyrins, **19** and **20**, were characterised by ^{1}H NMR spectroscopy, UV-Vis spectroscopy and high resolution mass spectrometry.

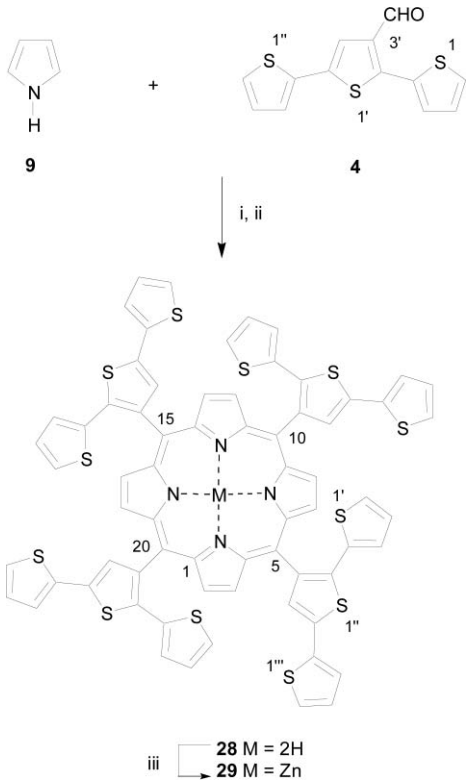
3. Synthesis and characterisation of Type V monomers

3.1 Tetra(β-thiophene) *meso*-substituted porphyrins. As with the α-thiophene-substituted porphyrins described earlier (Section 2.1), the commercial availability of 3-formylthiophene has facilitated the synthesis and study of analogous β-thiophene *meso*-appended porphyrins.[16d,21] Unfortunately, few of these literature reports provide detailed experimental procedures. It is clear that condensation of pyrroles **9** or **23** with 3-formylthiophene **2** has been employed to generate porphyrins of type **21** and **24**, respectively (Scheme 4).

Recently, in an attempt to improve the accessibility and yields of aryl *meso*-substituted porphyrins, Wheelhouse and Shi[22] have developed a divergent synthesis that utilises metal-mediated coupling protocols. Coupling of aryl boronic acids, such as thiophene-3-boronic acid **27**, with the tetrabromide porphyrin platform **26** under typical Suzuki coupling conditions gave the free base porphyrin **21** in surprisingly good yield (52%). This approach may serve as an alternative to classical condensation routes when commercial or known literature procedures to aryl boronic acids are available (see also Section 2.1). As observed with simple free-base thiophene-appended porphyrins described earlier, metallations with Cu, Zn or Ni have been shown to proceed smoothly, affording metalloporphyrins in essentially quantitative yields.

Interestingly, unlike the α-oligothiophene *meso*-substituted series (Section 2.1), there have been no reports of higher β-oligothiophene homologues. The contributing factor has been the lack of reported syntheses of β-formyloligothiophenes. However, the recent development and advancement of metal-catalysed carbon–carbon bond-forming reactions has resolved this problem, enabling the synthesis of complex polyaromatic materials.[23] Having recently devised a synthetic route to 3′-formylterthiophene **4** for conducting polymer application, we set out to establish whether this hindered aldehyde would give rise to a tetra-*meso*-substituted porphyrin using the condensation method.

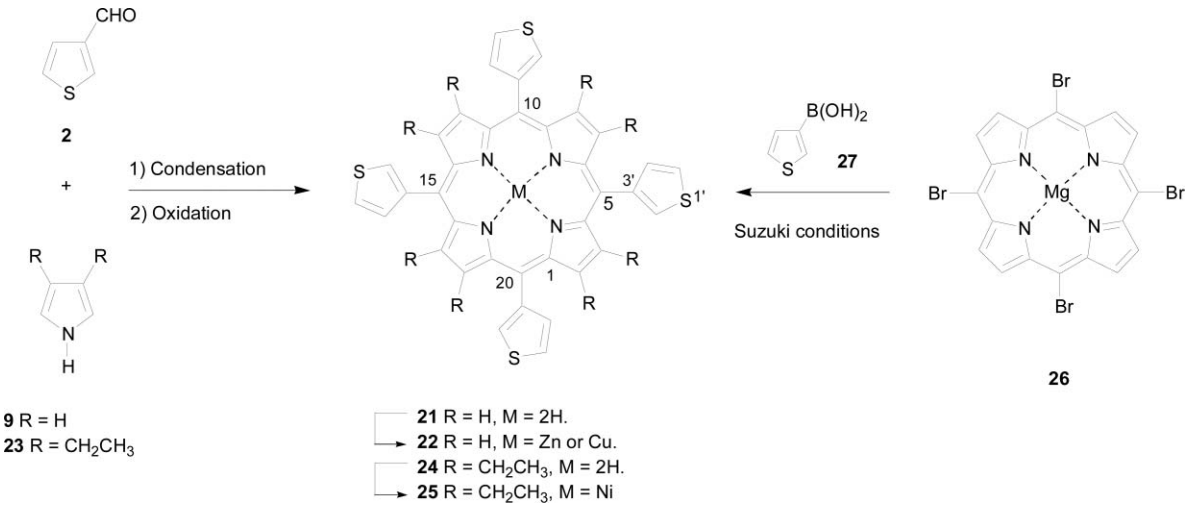
Treatment of aldehyde **4** and pyrrole **9** with trifluoroacetic acid as described by Lindsey[17b] encouragingly afforded the desired free-base tetra-substituted porphyrin **28**, although in disappointingly low yield (17%). However, using the same procedure, but employing a catalytic amount of the Lewis acid boron trifluoride diethyl etherate, resulted in a marked improvement in yield (34%) (Scheme 5). Analysis of the ^{1}H NMR spectrum of



Scheme 5 Synthesis of tetra(β-terthiophene) *meso*-substituted porphyrins. *Reagents and conditions*: Compound **28** i) DCM, $BF_3{\cdot}Et_2O$; ii) *p*-chloranil, heat, NEt_3; iii) $Zn(OAc)_2{\cdot}2H_2O$, MeOH, $CHCl_3$, RT.

pure **28** indicated a very complex array of signals. Due to the size and unsymmetrical nature of the terthiophene aldehyde moiety, atropisomers were not unexpected.[24,25]

Numerous attempts to separate or isolate the individual atropisomers by a variety of methods proved unsuccessful. Atropisomers with bulky aryl-substituted porphyrins are common, and in cases where certain functionalities are present, for example hydroxyl or amino groups, chromatographic separation can be accomplished.[25] Unfortunately, no separation of the isomers of **28** could be achieved by TLC or by performing careful column chromatography under a variety of eluant solvent systems. Neither was it possible to obtain eluant fractions that were enriched in any one isomer so that key signals could be attributed to a specific isomer. Also, attempts to selectively crystallise one of the isomers from solution were unsuccessful, resulting in co-precipitation. As a last resort, interconversion



Scheme 4 Synthesis of tetra(β-thiophene) *meso*-substituted porphyrins.

of the mixture of isomers into a major thermodynamically favorable form was attempted. Atropisomers of **28** were studied under variable temperature ^{1}H NMR spectroscopy by gradually heating in deuterobenzene to 79 °C and then cooling to room temperature, but no change in the product distribution could be observed. This is not at all surprising, as examination of **28** using CPK modelling studies indicate that rotation of the bond joining the central thiophene ring to the porphyrin system is clearly prevented due to the interaction of the β-pyrrolic protons with the outer thiophene rings of the terthiophene system.

Detailed 1D and 2D NMR studies were performed on a pure sample of the atropisomers of **28**. The most distinguishable feature of the ^{1}H NMR spectrum is the group of singlets that occurs in the region 7.76–7.90 ppm (Fig. 2). These signals can only attributed to the uncoupled H4″ located on the central thiophene ring of the terthiophene system. The significance of the six singlets of different intensities can be rationalised in terms of the formation of four atropisomers.

The isomers can be defined according to whether the H4″ lies above or below the plane of the porphyrin ring.[26] From these representations it is possible to determine the expected number of signals from H4″ that will be observed in each isomer. We expected six signals, which is in agreement with the observed signals, further confirming the presence of these four atropisomers.[24] However, since we cannot conclusively assign the signals observed directly to each isomer, it is not possible to determine whether the condensation of pyrrole **9** and terthiophene aldehyde **4** favors the formation of any particular one of these isomers or whether the expected statistical mixture (1 : 4 : 2 : 1) is formed. Also evident from the long-range COSY spectrum is the five-bond coupling between H3‴ of the outer thiophene ring, which lies closest to the H4″ of the central thiophene ring (Fig. 2).[10c]

Attempts to metallate **28** proved surprisingly difficult. The reaction of **28** with zinc acetate under normal conditions was slow. Use of excess zinc acetate and performing the reaction at elevated temperatures still did not drive the reaction to completion, as indicated by TLC, although it gave satisfactory yields (65%) of metalloporphyrin **29** and also returned unreacted free-base porphyrin. Based on the CPK modelling studies and NMR information described earlier, it appears that metallation of some of these atropisomers may be slower than others, due to the steric constraints imposed by the terthiophene moieties.

3.2 5,15-Bis(β-thiophene)porphyrins. During the study on 5,15-bis(α-thiophene)substituted porphyrin **17** (Section 2.2) Armiger and Lash[20] also published a synthesis of the 5,15-bis(β-thiophene)substituted porphyrin **30** analogue (Scheme 6). Using MacDonald-type conditions, reaction of 3-formylthiophene **2** with the dipyrrylmethane derivative **16** gave the porphyrin **30** after purification in only 16% yield.

Our initial efforts to synthesise **31**, using the reaction conditions developed for 5,15-bis(α-thienyl)substituted porphyrin **17**, gave only marginally better yields (23%). However, applying Lindsey's conditions with trifluoroacetic acid was useful, giving the desired porphyrin **31** in a respectable yield (53%) after purification. Characterisation of **31** was achieved by ^{1}H NMR, UV/Visible and FAB-HRMS spectroscopy, and the data were consistent with the structure of **31**. Analysis of the ^{1}H NMR spectrum of **31** showed it to be very similar to that of α-thiophene porphyrin **17**. The most significant difference between the NMR data of these compounds was that the thiophene protons, H2′, H4′ and H5′, of **31** are magnetically equivalent, occurring at 7.77 ppm, in contrast to several multiplets observed for H3′, H4′ and H5′ of **17**. Interestingly, from the data of **31** and **17** there is not sufficient evidence to suggest that these compounds exhibit atropisomerism.

Having optimised the condensation conditions for the formation of **31**, we then focused our attention on the terthiophene homologue **32** (Scheme 7). Employing Lindsey's conditions, reaction of dipyrrylmethane **18** and terthiophene aldehyde **4** with trifluoroacetic acid gave the 5,15-bis(β-terthiophene)porphyrin **32** in moderate yield (41%) as a mixture of atropisomers. As with the tetra-*meso*-(β-terthiophene)porphyrin **28** described earlier, all

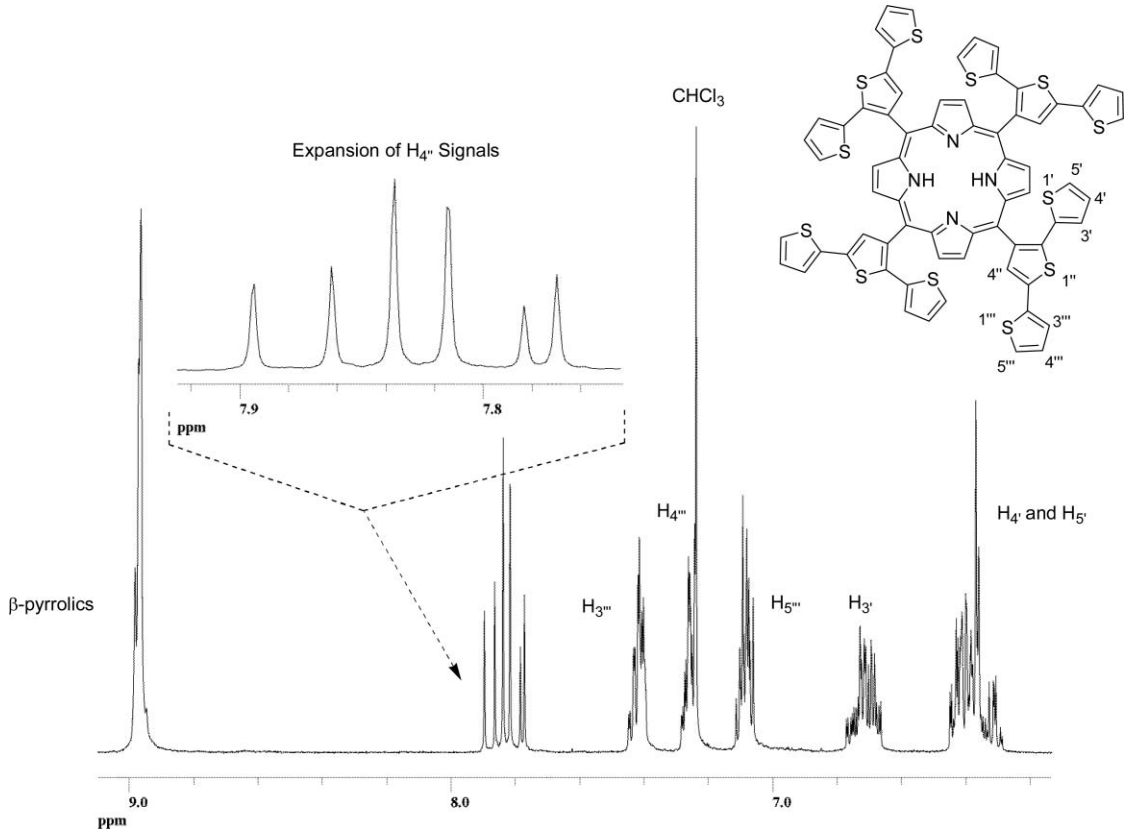
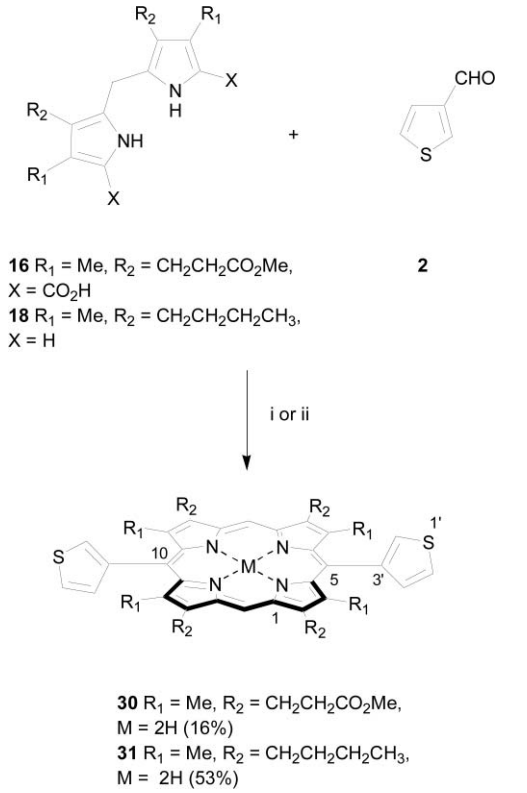


Fig. 2 Expanded aromatic region of 400 MHz ^{1}H NMR spectrum of tetra(β-terthiophene)porphyrin **28**.



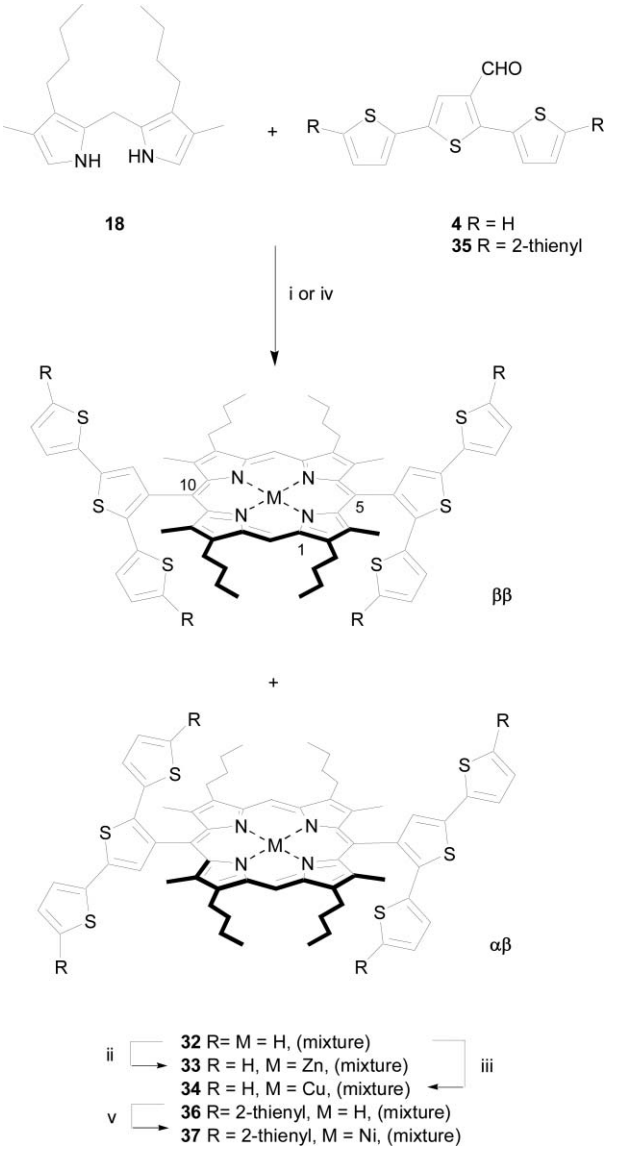
Scheme 6 Synthesis of Type V 5,15-bis(β-thiophene)porphyrin monomers. *Reagents and conditions*: Compound **30**, i) EtOH, trichloroacetic acid, RT, then THF, DDQ; Compound **31**; ii) DCM, TFA, RT, then DBU, *p*-chloranil, NEt_3.

attempts to separate or interconvert the mixture to a single isomer were unsuccessful. Analysis of the free-base porphyrin by ^{1}H NMR spectroscopy indicated duplication of certain key signals, confirming a statistical mixture of **32** ββ and **32** αβ. Also substantially different to that of the tetra-substituted compound **28**, was the ease by which this free-base porphyrin **32** could be metallated with zinc or copper, giving 100% and 83% yields, respectively.

The ability to control porphyrin-to-thiophene ratios was further enhanced by the synthesis of the hitherto unknown 3″-formyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-pentathiophene **35**.[27] This provided the precursor to the next homologue in the β-oligothiophene disubstituted series **36**. Unfortunately, employing the conditions that proved extremely successful in the synthesis of **17** and **32** did not lead to the formation of any appreciable quantities of **36**. Instead, condensation of dipyrrylmethane **18** with the aldehyde **35** with trace amounts of boron trifluoride diethyl etherate gave high yields (53%) of the desired porphyrin **36**. As expected, the ^{1}H NMR spectrum of the bis(β-pentathiophene)porphyrin **36** is extremely complex due to the presence of the additional thiophene rings and the formation of the *syn*- and *anti*-isomers, **36** ββ and **3** αβ. Surprisingly, unlike any of the free-base porphyrins mentioned in this paper, **36** was isolated as a reddish solid more characteristic of the oligothiophene component; this is in stark contrast to the usual purple colour observed for porphyrins. As with lower homologues **17** and **32**, the free-base porphyrin **36** was easily metallated with nickel (90%). Once again, as with the other atropisomers reported in this paper, separation of the atropisomers proved impossible.

Conclusion

By considering structural morphology and synthetic strategy, we have designed and developed synthetic routes to three of the five key monomeric types. The versatility of each synthetic route is realised by the ease by which we can "tune" individual components and thereby adjust the physical, chemical and electro-



Scheme 7 Synthesis of Type V 5,15-bis(β-terthiophene)porphyrin monomers. *Reagents and conditions*: Compound **32**, i) DCM, TFA, RT, then DBU, *p*-chloranil, RT, NEt_3; Compound **33**; ii) $Zn(OAc)_2{\cdot}2H_2O$, MeOH, $CHCl_3$, RT; iii) $Cu(OAc)_2{\cdot}H_2O$, MeOH, $CHCl_3$, heat. Synthesis of Type V 5,15-bis-(β-pentathiophene)porphyrin monomers. *Reagents and conditions*: Compound **36**, i) DCM, $BF_3{\cdot}Et_2O$, RT, then *p*-chloranil, NEt_3; ii) $Ni(OAc)_2{\cdot}4H_2O$, MeOH, $CHCl_3$, heat.

chemical properties of the monomeric unit and polymer. Our current efforts show there is indeed a balance between synthetic efficiency and structural complexity that needs to be addressed when making polymers from such hybrid materials.[28,29] Further research is also focused on testing these different hybrid materials in other applications, involving electrocatalysis and sensor devices. Results from these ongoing studies will be published in the near future.

Experimental

All porphyrin reactions were performed under an inert atmosphere of nitrogen or argon, using dry degassed analytical grade solvents[30] and in the absence of light. Bis(3-butyl-4-methyl-2-pyrryl)methane (DPM) **18** was prepared according to the method of Sessler and co-workers.[25c,f] Porphyrin phosphonium salts,[9c] triphenyl[5,10,15,20-tetraphenylporphyrin-2-yl)methyl]-phosphonium chloride (TPPps) **1** triphenyl[(5,10,15,20-tetrakis-(3,5-dimethylphenyl)porphyrin-2-yl)methyl]phosphonium chloride (TXPps) **6**, and 3′-formyl-2,2′;5′,2″-terthiophene **4**[10c] were prepared according to literature procedures. Thin layer

chromatography (TLC) was performed using precoated silica gel plates (Merck Kieselgel $60F_{254}$), while preparative column chromatography employed silica gel (0.032–0.063 mm, Merck Kieselgel 60). All solid precipitates were separated by filtration or centrifugation, collected and then dried under high vacuum overnight. Melting point determinations were performed on a Cambridge Instruments Kofler hotstage. All oligothiophene-porphyrin derivatives reported in this article have melting points that are higher than 280 °C, which is the upper limit of this instrument.

^{1}H NMR spectra were recorded on JEOL JMN-GX270 (270 MHz) or Bruker Avance (400 MHz) spectrometers, and signals are quoted in ppm relative to tetramethylsilane or residual chloroform (7.25 ppm). Where products are obtained as inseparable mixtures of atropisomers, 2D LRCOSY and NOESY experiments were employed to resolve the chemical shifts of key structural components. However, the NMR data is presented to aid the identification of these products, since it is not possible to unambiguously assign the signals to the specific isomers. Electronic absorption spectra were obtained using a Shimadzu UV-3101PC UV-Vis-NIR-Scanning Spectrophotometer. Mass spectra were recorded using a Varian VG70–250S double focusing magnetic sector mass spectrometer and samples analysed by FAB-HRMS were supported in a *p*-nitrobenzyl alcohol matrix.

Synthesis of Type I monomers

***Trans*-1-(2′-(5′,10′,15′,20′-tetraphenylporphyrinyl))-2-(3″-thienyl)ethene 3.** A mixture of 3-formylthiophene **2** (336 mg, 3.00 mmol, 3 equiv.) and TPPps **1** (925 mg, 0.999 mmol) in anhydrous dichloromethane (100 mL) was treated with dry triethylamine (0.69 mL, 505 mg, 4.99 mmol) and left to stir at ambient conditions. After 2 h another portion of triethylamine (0.69 mL, 505 mg, 4.99 mmol) was added and stirring continued for a further 2 h. After this period the reaction mixture was washed thoroughly with a 5% solution of aqueous HCl (2 × 50 mL), a 10% solution of sodium thiosulfate (2 × 50 mL), water (100 mL) and dried ($MgSO_4$). The mixture was then concentrated to give a purple–brown solid that consisted of a mixture of geometric isomers as indicated by the proton NMR spectrum. This crude product was dissolved in dichloromethane (50 mL) and stirred in the presence of iodine (756 mg, 2.98 mmol) at RT for 24 h. The solution was washed with saturated sodium thiosulfate solution (50 mL), water (100 mL), then dried ($MgSO_4$) and the solvent removed under reduced pressure. The resulting solid was subjected to column chromatography (50 mm^{dia} × 150 mm) with constant elution with dichloromethane–hexane (1 : 2). The material was collected and recrystallised from dichloromethane–methanol to afford the all-*trans TPP-thiophene* **3** as a purple–brown microcrystalline solid (512 mg, 70%). λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 404 sh (4.6), 423 (5.6), 520 (4.7), 565 (4.4), 598 (4.3), 656 (4.1); δ_H (270 MHz, $CDCl_3$) −2.61 (br s, 2H, NH); 6.76 (d, 1H, *J* 16.2 Hz, H 1); 6.92–6.95 (m, 1H, thiophene H); 7.15–7.19 (m, 1H, thiophene H); 7.26–7.29 (m, 1H, thiophene H); 7.32 (d, 1H, *J* 16.2 Hz, H 2); 7.68–7.87 (m, 12H, ArH); 8.15–8.27 (m, 8H, ArH); 8.70 and 8.80 (ABq, 2H, *J* 4.9 Hz, β-pyrrolic H); 8.76 and 8.80 (ABq, 2H, *J* 4.9 Hz, β-pyrrolic H); 8.83 (s, 2H, β-pyrrolic H); 8.97 (s, 1H, H 3′); *m/z* (FAB-LRMS) 723 (100%, MH^+); *m/z* (FAB-HRMS) Found: 722.2470 (MH^+, $C_{50}H_{35}N_4S$ requires 722.2504).

***Trans*-1-(5′,10′,15′,20′-tetraphenylporphyrin-2′-yl)-2-((2″,2‴:5‴,2⁗-terthiophen)-3‴-yl)ethene 5.** A stirred solution of 3′-formyl-2,2′:5′,2″-terthiophene **4** (235 mg, 0.850 mmol) and TPPps **1** (786 mg, 0.849 mmol) dissolved in dry 1,2-dichloroethane (50 mL) was treated with DBU (254 μL, 258 mg, 1.70 mmol, 2 equiv.). The mixture was heated under reflux overnight by irradiation with a tungsten lamp source. After this period the solvent was removed *in vacuo* and the product crystallised from a hot solution of chloroform–methanol to give the all-*trans TPP-terthiophene* **5** as a purple solid (527 mg, 70%). λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 311 sh (26), 423 (188), 524 (17.3), 567 (11.2), 600 (7.56), 657 (3.61); δ_H (270 MHz, $CDCl_3$) −2.62 (br s, 2H, NH); 6.81 (d, 1H, *J* 16.0 Hz, H 1); 6.95 (s, 1H, H 4‴); 7.10–7.20 (m, 2H, H 4″ and 4⁗); 7.25 (dd, 1H, *J* 3.4, 1.2 Hz, H 3″); 7.28 (dd, 1H, *J* 3.4, 1.2 Hz, H 3⁗); 7.39 (dd, 1H, *J* 5.2, 1.2 Hz, H 5⁗); 7.44 (dd, 1H, *J* 5.2, 1.2 Hz, H 5″); 7.66 (d, 1H, *J* 16.0 Hz, H 2); 7.70–7.91 (m, 15H, ArH); 7.95–8.04 (m, 1H, ArH); 8.16–8.30 (m, 8H, ArH); 8.73–8.89 (m, 6H, β-pyrrolic H); 8.90 (s, 1H, H 3′); *m/z* (FAB-LRMS) 887 (100%, MH^+); *m/z* (FAB-HRMS) Found: 887.2373 (MH^+, $C_{58}H_{39}N_4S_3$ requires 887.2337).

***Trans*-1-(2′-(5′,10′,15′,20′-tetrakis(3″,5″-dimethylphenyl)porphyrinyl))-2-([2‴,2⁗:5⁗,2⁗′-terthiophen]-3⁗-yl)ethene 7.** To a solution of TXPps **6** (100 mg, 96.4 μmol) and 3′-formyl-2,2′:5′,2″-terthiophene **4** (71.9 mg, 260 μmol, 2.7 equiv.) in anhydrous toluene (5 mL) heated at reflux was added DBU (43 μL, 43.8 mg, 0.288 mmol, 3 equiv.). After 30 min the mixture was cooled and the solvent removed under reduced pressure. The crude product was subjected to column chromatography (27 mm^{dia} × 100 mm) eluting with dichloromethane–hexane (3 : 1). The first major purple band was collected (R_f = 0.50, dichloromethane–hexane (1 : 1)) and concentrated to give a solid. This material was dissolved in dichloromethane and precipitated from solution by the addition of methanol to afford the all-*trans TXP-terthiophene* **7** as a purple powder (80.3 mg, 83%). λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 311 (34.4), 426 (255), 527 (23.6), 568 (14.5), 601 (9.20), 660 (3.94); δ_H (400 MHz, $CDCl_3$) −2.60 (br s, 2H, NH); 2.59 (s, 18H, CH_3); 2.61 (s, 6H, CH_3); 6.80 (d, 1H, *J* 16.0 Hz, H 1); 7.02 (s, 1H, H 4⁗′); 7.12 (dd, 1H, *J* 5.1, 3.6 Hz, H 4⁗″); 7.14 (dd, 1H, *J* 5.1, 3.6 Hz, H 4‴); 7.26 (dd, 1H, *J* 3.6, 1.1 Hz, H 3‴); 7.28 (dd, 1H, *J* 3.6, 1.1 Hz, H 3⁗″); 7.37 (dd, 1H, *J* 5.1, 1.1 Hz, H 5⁗″); 7.38–7.42 (m, 3H, *p*-ArH); 7.41 (dd, 1H, *J* 5.1, 1.1 Hz, H 5‴); 7.60 (br s, 1H, *p*-ArH); 7.65 (d, 1H, *J* 16.0 Hz, H 2); 7.83 (br s, 5H, *o*-ArH); 7.87 (br s, 3H, *o*-ArH); 8.80 and 8.81 (ABq, 2H, *J* 4.8 Hz, H 7′and 8′); 8.83 and 8.86 (ABq, 2H, *J* 4.8 Hz, H 17′ and 18′); 8.85 (s, 2H, H 12′ and 13′); 9.02 (s, 1H, H 3′); *m/z* (FAB-LRMS) 999 (100%, MH^+); *m/z* (FAB-HRMS) Found: 999.3534 (MH^+, $C_{66}H_{55}N_4S_3$ requires 999.3589).

***Trans*-1-(2′-(5′,10′,15′,20′-tetrakis(3″,5″-dimethylphenyl)porphyrinato zinc(II)yl))-2-([2‴,2⁗:5⁗,2⁗′-terthiophen]-3⁗-yl)ethene 8.** A solution of $Zn(OAc)_2 \cdot 2H_2O$ (11.9 mg, 54 μmol, 1.2 equiv.) in methanol (1 mL) was added to a solution of *trans*-TXP-terthiophene **7** (45.0 mg, 45.0 μmol) in chloroform (4.5 mL) with stirring at RT for 1 h. The crude product was precipitated with methanol and the resulting solid was recrystallised from dichloromethane–methanol to give *Zn-TXP-terthiophene* **8** (41.3 mg, 86%) as a purple microcrystalline solid. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 310 (34.7), 353 (31.1), 430 (227), 561 (23.4), 597 (10.7); δ_H (400 MHz, $CDCl_3$) 2.59 (s, 6H, CH_3); 2.60 (s, 12H, CH_3); 2.61 (s, 6H, CH_3); 6.82 (dd, 1H, *J* 15.7, 0.8 Hz, H 1); 7.04 (s, 1H, H 4⁗′); 7.12–7.15 (m, 2H, thiophene H); 7.26–7.28 (m, 2H, thiophene H); 7.37–7.41 (m, 2H, thiophene H); 7.39–7.42 (m, 3H, *p*-ArH); 7.61 (s, 1H, *p*-ArH); 7.62 (d, 1H, *J* 15.7 Hz, H 2); 7.82 (s, 2H, *o*-ArH); 7.84 (s, 4H, *o*-ArH); 7.87 (s, 2H, *o*-ArH); 8.92 and 8.95 (m, 4H, β-pyrrolic H); 8.97 and 9.00 (ABq, 2H, *J* 4.7 Hz, H 17′ and 18′); 9.13 (d, 1H, *J* 0.8 Hz, H 3′); *m/z* (FAB-LRMS) cluster at 1060–1066, 1060 (85%, M^+); *m/z* (FAB-HRMS) Found: 1060.2542 (M^+, $C_{66}H_{52}N_4S_3Zn$ requires 1060.2646).

Synthesis of Type II monomers

5,15-Bis(2′-thienyl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphine 19. *p*-Toluenesulfonic acid monohydrate (30.2 mg, 0.159 mmol, 0.25 equiv.) was added to a solution of 2-formylthiophene **10** (71.2 mg, 0.635 mmol) and dipyrrylmethane

18 (200 mg, 0.698 mmol, 1.1 equiv.) in methanol (8 mL) at RT. The reaction was sealed and stirred for 12 h before removing the solvent under reduced pressure. The residue was dissolved in dichloromethane (20 mL) and *p*-chloranil (342 mg, 1.39 mmol, 2.2 equiv.) was added and the mixture stirred for a further 2.5 h at RT. Next a saturated solution of sodium thiosulfate (50 mL) containing triethylamine (500 μL) was added and the mixture stirred vigorously for 1.5 h. The organic layer was separated and dried ($MgSO_4$) and the product was precipitated from a solution with methanol (twice), filtered and dried under high vacuum to give the *5,15-(di-a-thiophene)porphyrin* **19** (155 mg, 65%) as a dark purple powder. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 409 (194), 510 (14.2), 545 (6.74), 578 (5.81), 629 (3.36); δ_H (270 MHz, $CDCl_3$) −2.31 (br s, 2H, NH); 1.10 (t, 12H, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 1.75 (app sext, 8H, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 2.10–2.25 (m, 8H, $CH_2CH_2CH_2CH_3$); 2.72 (s, 12H, β-pyrrolic CH_3); 4.00 (t, 8H, *J* 7.6 Hz, $CH_2CH_2CH_2CH_3$); 7.48 (dd, 2H, *J* 5.2, 3.4 Hz, H 4′); 7.75 (dd, 2H, *J* 3.4, 0.9 Hz, H 3′); 7.82 (dd, 2H, *J* 5.2, 0.9 Hz, H 5′); 10.25 (s, 2H, H 10 and 20); *m/z* (FAB-LRMS) 756 (100%, MH^+); *m/z* (FAB-HRMS) Found: 755.4130 (MH^+, $C_{48}H_{59}N_4S_2$ requires 755.4181).

5,15-Bis(2′-thienyl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato zinc(II) 20. A solution of $Zn(OAc)_2 \cdot 2H_2O$ (35 mg, 0.159 mmol, 2 equiv.) dissolved in methanol (1 mL) was added to a stirred solution of porphyrin **19** (60.0 mg, 79.5 μmol) in chloroform (10 mL) at RT. The reaction mixture was monitored by TLC and judged complete after 10 min (R_f = 0.1; Al_2O_3, dichloromethane–hexane (1 : 3)), by the absence of any starting material **19**. The product was precipitated from the solution by the addition of methanol, filtered and dried under high vacuum to give the *zinc-metallated porphyrin* **20** (65.7 mg, 100%) as a purple microcrystalline solid. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 350 (17.9), 412 (369), 541 (17.5), 580 (14.7); δ_H (270 MHz, $CDCl_3$) 1.11 (t, 12H, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 1.74 (app sext, 8H, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 2.06–2.22 (m, 8H, $CH_2CH_2CH_2CH_3$); 2.66 (s, 12H, β-pyrrolic CH_3); 3.90 (t, 8H, *J* 7.6 Hz, $CH_2CH_2CH_2CH_3$); 7.49 (dd, 2H, *J* 5.2, 3.4 Hz, H 4′); 7.74 (dd, 2H, *J* 3.4, 0.9 Hz, H 3′); 7.82 (dd, 2H, *J* 5.2, 0.9 Hz, H 5′); 10.07 (s, 2H, H 10 and 20); *m/z* (FAB-LRMS) 817 (22, M^+), 756 (100%); *m/z* (FAB-HRMS) Found: 816.3217 (M^+, $C_{48}H_{56}N_4S_2Zn$ requires 816.3238).

Synthesis of Type IV monomers

5,10,15,20-Tetrakis([2′,2″:5″,2‴-terthiophen]-3″-yl)porphine 28. 3′-Formyl-2,2′:5′,2″-terthiophene **4** (158 mg, 0.572 mmol) and pyrrole **9** (39.65 μL, 0.572 mmol) were dissolved in degassed anhydrous dichloromethane (57 mL) at RT. Boron trifluoride diethyl etherate (7.0 μL, 57 μmol, 0.1 equiv.) was added and the solution stirred for 2 h. After this period, *p*-chloranil (105 mg, 0.429 mmol, 0.75 equiv.) was added and the solution stirred at reflux for 2 h. An excess of triethylamine was then added and the solvent removed under reduced pressure. The residue was subjected to column chromatography (37 mm^{dia} × 80 mm, dichloromethane–hexane (1 : 1)) collecting the first major porphyrin-coloured band (R_f = 0.15, dichloromethane–hexane (1 : 1)). The product was then precipitated from a solution of dichloromethane by addition of methanol, filtered and dried under high vacuum to give meso-*tetra(β-terthiophene)porphyrin* **28** (62.4 mg, 34%) as a purple powder containing an inseparable mixture of four atropisomers, as indicated by proton NMR spectroscopy. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 252 (43), 357 (100), 426 (220), 525 (21), 561 (6.4), 596 (7.5), 654 (1.7); δ_H (270 MHz, $CDCl_3$) −2.50, −2.47 (2 br s, NH); 6.30–6.47 (m, thiophene H); 6.66–6.79 (m, thiophene H); 7.06–7.13 (m, thiophene H); 7.23–7.30 (m, thiophene H); 7.39–7.46 (m, thiophene H); 7.77, 7.78, 7.82, 7.84, 7.86, 7.90 (6 s, H 4″); 8.93–9.00 (m, β-pyrrolic H); *m/z* (FAB-LRMS) 1295 (100%, MH^+); *m/z* (FAB-HRMS) Found: 1294.9798 (MH^+, $C_{68}H_{39}N_4S_{12}$ requires 1294.9823).

5,10,15,20-Tetrakis([2′,2″:5″,2‴-terthiophen]-3″-yl)porphyrinato zinc(II) 29. A solution of $Zn(OAc)_2 \cdot 2H_2O$ (9.3 mg, 42 μmol, 1.2 equiv.) in methanol (1 mL) was added to a solution of *meso*-tetra(terthiophene)porphyrin **28** (45.9 mg, 35.4 μmol) in chloroform (4.5 mL) with stirring at RT. After 1 h, two close-running coloured bands were observed by TLC, suggesting the metallation was incomplete. An additional portion of $Zn(OAc)_2 \cdot 2H_2O$ (6.2 mg, 28 μmol, 0.8 equiv.) in methanol (0.5 mL) was added and the reaction mixture was heated at reflux for 1 h. After this period, these two bands were still evident by TLC and the reaction was ceased. The solvent was removed *in vacuo* and the residue subjected to column chromatography (30 mm^{dia} × 200 mm, dichloromethane–hexane (1 : 1)), collecting the first coloured fraction. Recrystallisation of this material from dichloromethane–methanol gave recovered *free-base porphyrin* **28** (3.4 mg), as indicated by ^1H NMR. Further elution gave the major coloured fraction, which afforded a solid upon concentration. Recrystallisation of this material from dichloromethane–methanol gave the *zinc-metalled porphyrin* **29** (31.5 mg, 65%) as a purple powder. The ^1H NMR spectrum is consistent with the presence of four atropisomers. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 352 (97.3), 434 (264), 521 (7.91), 559 (28.3), 598 (6.18); δ_H (400 MHz, $CDCl_3$) 6.26–6.44 (m, thiophene H); 6.74–6.83 (m, thiophene H); 7.06–7.11 (m, thiophene H); 7.22–7.28 (m, thiophene H); 7.40–7.44 (m, thiophene H); 7.83, 7.84, 7.90, 7.91, 7.93, 7.94, (6 s, H 4″); 9.05–9.09 (m, β-pyrrolic H); *m/z* (FAB-LRMS) cluster at 1356–1364, 1356 (55%, M^+); *m/z* (FAB-HRMS) Found: 1355.8801 (M^+ for $C_{68}H_{36}N_4S_{12}Zn$ requires 1355.8880).

5,15-Bis(3′-thienyl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphine 31. To a stirred solution of 3-formylthiophene **2** (30.6 μL, 0.349 mmol) and dipyrrylmethane **18** (100 mg, 0.349 mmol) in degassed anhydrous dichloromethane (35 mL) at RT was added trifluoroacetic acid (26.9 μL, 0.349 mmol, 1 equiv.). At the first sign of baseline material by TLC (∼15 min; silica gel, dichloromethane) the reaction was quenched by the addition of DBU (52.2 μL, 0.349 mmol, 1 equiv.). *p*-Chloranil (214 mg, 0.873 mmol, 2.5 equiv.) was then added and the solution stirred for 4 h at RT. Next, triethylamine (36 μL, 0.258 mmol) was added and the reaction stirred vigorously for 1.5 h. After this period additional triethylamine (723 μL, 5.19 mmol) was added and the reaction stirred for 15 min (a complex forms with *p*-chloranil which is soluble in methanol). The product was then precipitated from solution by the addition of methanol, filtered and dried under high vacuum to give *5,15-(di-β-thiophene)porphyrin* **31** (69.3 mg, 53%) as a purple crystalline solid. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 408 (208), 507 (19.8), 542 (9.1), 574 (10.5), 627 (5.4), 674 (3.7); δ_H (270 MHz, $CDCl_3$) −2.41 (br s, 2H, NH); 1.12 (t, 12H, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 1.84 (app sext, 8H, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 2.13–2.28 (m, 8H, $CH_2CH_2CH_2CH_3$); 2.66 (s, 12H, β-pyrrolic CH_3); 4.03 (t, 8H, *J* 7.6 Hz, $CH_2CH_2CH_2CH_3$); 7.77 (s, 6H, thiophene H); 10.26 (s, 2H, H 10 and 20); *m/z* (FAB-LRMS) 755 (100%, MH^+); *m/z* (FAB-HRMS) Found: 755.4162 (MH^+, $C_{48}H_{59}N_4S_2$ requires 755.4181).

5,15-Bis([2′,2″:5″,2‴-terthiophen]-3″-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin 32. To a stirred solution of 3′-formyl-2,2′:5′,2″-terthiophene **4** (96.5 mg, 0.349 mmol) and dipyrrylmethane **18** (100 mg, 0.349 mmol) in degassed dry dichloromethane (35 mL) at ambient conditions was added trifluoroacetic acid (26.9 μL, 0.349 mmol, 1 equiv.). At the first sign of baseline material by TLC (∼15 min; silica gel, dichloromethane) the reaction was quenched by the addition of DBU (52.2 μL, 0.349 mmol, 1 equiv.) and then treated with *p*-chloranil (214 mg, 0.873 mmol, 2.5 equiv.) and stirred for 4 h at RT. After this period triethylamine (36 μL, 0.258 mmol) was added and the reaction mixture stirred vigorously for 1 h. Then excess triethylamine (723 μL, 5.19 mmol) was added and the

reaction stirred for 15 min. The product was then precipitated from solution by the addition of methanol, collected and dried under high vacuum to give *5,15-(di-β-terthiophene)porphyrin* **32** (77 mg, 41%) as an inseparable mixture of atropisomers. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 415 (203), 511 (17.8), 546 (7.06), 577 (7.59), 630 (3.23); δ_H (400 MHz, $CDCl_3$) −2.31, −2.30 (2 br s, NH); 1.07 (t, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 1.65–1.78 (app sext, $CH_2CH_2CH_2CH_3$); 2.11–2.26 (app pent, $CH_2CH_2CH_2CH_3$); 2.90 (s, β-pyrrolic CH_3); 3.90–4.10 (m, $CH_2CH_2CH_2CH_3$); 6.40–6.48 (m, H 4′ and 5′); 6.75, 6.79 (2 dd, *J* 3.4, 1.5 Hz, H 3′); 7.13, 7.14 (2 dd, *J* 5.2, 3.6 Hz, H 4‴); 7.29, 7.30 (2 dd, *J* 5.2, 1.1 Hz, H 5‴); 7.45, 7.46 (2 dd, *J* 3.6, 1.1 Hz, H 3‴); 7.63 (m, H4″); 10.22, 10.23 (2 s, H 10 and 20); *m/z* (FAB-LRMS) 1083 (100%, MH^+); *m/z* (FAB-HRMS) Found: 1083.3719 (MH^+ for $C_{64}H_{67}N_4S_6$ requires 1083.3690).

5,15-Bis([2′,2″:5″,2‴-terthiophen]-3″-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinato zinc(II) 33. A solution of $Zn(OAc)_2{\cdot}2H_2O$ (42.9 mg, 196 μmol, 1.2 equiv.) in methanol (1 mL) was added to a solution of 5,15-(di-β-terthiophene)-porphyrin **32** (177 mg, 163 μmol) in chloroform (18 mL) with stirring at RT. The reaction was deemed complete by TLC (R_f = 0.25, silica, dichloromethane–hexane (1 : 2)) after 30 min. The crude product was precipitated from solution by the addition of methanol, and the resulting solid was recrystallised from dichloromethane–methanol to give *zinc-metallated porphyrin* **33** (189 mg, 100%) as a brick-red powder. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 353 (63.2), 418 (336), 504 (4.51), 543 (21.6), 581 (13.4); δ_H (400 MHz, $CDCl_3$) 1.08 (t, *J* 7.3 Hz, $CH_2CH_2CH_2CH_3$); 1.68–1.79 (app sext, $CH_2CH_2CH_2CH_3$); 2.13–2.21 (app pent, $CH_2CH_2CH_2CH_3$); 2.92 (s, β-pyrrolic CH_3); 3.90–4.05 (m, $CH_2CH_2CH_2CH_3$); 6.34–6.44 (m, thiophene H); 6.78–6.80 (m, thiophene H); 7.135, 7.137 (2 dd, *J* 5.2, 3.7 Hz, H 4‴); 7.293, 7.298 (2 dd, *J* 5.2, 1.2 Hz, H 5‴); 7.459, 7.463 (2 dd, *J* 3.7, 1.2 Hz, H 3‴); 7.67, 7.70 (2 s, H 4″); 10.19 (s, H 10 and 20); *m/z* (FAB-LRMS) cluster at 1143–1151, 1144 (80%, M^+); *m/z* (FAB-HRMS) Found: 1144.2791 (M^+, $C_{64}H_{64}N_4S_6Zn$ requires 1144.2747).

5,15-Bis([2′,2″:5″,2‴-terthiophen]-3″-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinato copper(II) 34. A solution of $Cu(OAc)_2{\cdot}H_2O$ (111 mg, 508 μmol, 1.2 equiv.) in methanol (10 mL) was added to a solution of 5,15-(di-β-terthiophene)-porphyrin **32** (500 mg, 461 μmol) in chloroform (50 mL) and heated under reflux. After 15 h, TLC analysis indicated that all of the free-base porphyrin **32** had been metallated. The solvent was removed *in vacuo* and the residue subjected to column chromatography (37 mm^{dia} × 90 mm, dichloromethane–hexane (1 : 2)) and the major red-coloured band collected. Recrystallisation of this material from dichloromethane–methanol gave the *copper-metallated porphyrin* **34** (438 mg, 83%) as a purple solid. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 414 (379), 536 (22.0), 574 (20.3); *m/z* (FAB-LRMS) cluster at 1142–1149, 1143 (90%, M^+); *m/z* (FAB-HRMS) Found: 1143.2753 (M^+, $C_{64}H_{64}N_4CuS_6$ requires 1143.2751).

2,8,12,18-Tetra-*n*-butyl-3,7,13,17-tetramethyl-5,15-bis[2′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′]quinquethiophen-3‴-yl-porphyrin 36. A stirred solution of 3″-formyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗]quinquethiophene **35** (154 mg, 349 μmol) and dipyrrylmethane **18** (100 mg, 349 μmol) in degassed dry dichloromethane (35 mL) at RT was treated with boron trifluoride diethyl etherate (1 mL of 0.07 M in dichloromethane, 0.2 equiv.). After 110 min, *p*-chloranil (214 mg, 873 μmol, 2.5 equiv.) was added and the solution stirred for 3 h. After this period, excess triethylamine (1 mL) was added and reaction stirred vigorously for 15 min. The crude product was then precipitated from solution by the addition of methanol and collected on a sintered glass funnel (#4). The crude solid was subjected to column chromatography (37 mm^{dia} × 210 mm, chloroform–hexane (1 : 1)) and the major orange-coloured band was collected. Recrystallisation of this material from chloroform–methanol gave a red powder consisting of a mixture of *syn* and *anti* isomers (∼1 : 1 by ^{1}H NMR) of *5,15-(di-β-quinquethiophene)porphyrin* **36** (138 mg, 56%). λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 252 (35.6), 418 (255), 512 (19.7), 547 (7.57), 577 (8.16), 631 (2.91); δ_H (400 MHz, $CDCl_3$) −2.30 (br s, NH); 1.056, 1.060 (2 t, *J* 7.4 Hz, $CH_2CH_2CH_2CH_3$); 1.67–1.77 (app sext, $CH_2CH_2CH_2CH_3$); 2.14–2.22 (app pent, $CH_2CH_2CH_2CH_3$); 2.93 (s, β-pyrrolic CH_3); 3.92–4.08 (m, 16H, $CH_2CH_2CH_2CH_3$); 6.129, 6.322 (2 dd, 2H, *J* 3.6, 1.0 Hz, H 3′); 6.41–6.51 (3 m, H 4′, 3″, and 4″); 6.78, 6.83 (2 dd, *J* 5.0, 1.0 Hz, H 5′); 6.98–7.01 (m, thiophene H); 7.16–7.23 (m, thiophene H); 7.32, 7.34 (2 d, *J* 3.8 Hz, H 3⁗); 7.54, 7.57 (2 s, H 4‴); 10.248, 10.258 (2 s, H 10 and 20); *m/z* (FAB-LRMS) cluster at 1409–1416, 1411 (100%, M^+); *m/z* (FAB-HRMS) Found: 1411.3199 (MH^+, $C_{80}H_{75}N_4S_{10}$ requires 1411.3190).

2,8,12,18-Tetra-*n*-butyl-3,7,13,17-tetramethyl-5,15-bis[2′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′]quinquethiophen-3‴-yl-porphyrinato nickel(II) 37. A solution of $Ni(OAc)_2{\cdot}4H_2O$ (65 mg, 262 μmol, 10 equiv.) in methanol (2 mL) was added to a solution of 5,15-(di-β-quinquethiophene)porphyrin **36** (37 mg, 26.2 μmol) in chloroform (10 mL) which was heated at reflux. After 23 h, TLC analysis indicated that all of the free-base porphyrin **36** had been metallated. The solvent was removed *in vacuo* and the residue was subjected to column chromatography (25 mm^{dia} × 270 mm, dichloromethane–hexane (1 : 2)) and the major red-coloured band collected. This crude material was recrystallised from chloroform–methanol to give the *nickel-metallated porphyrin* **37** (36 mg, 90%) as a red powder. Analysis of the ^{1}H NMR spectrum indicated a mixture of atropisomers. λ_{max}/nm (CH_2Cl_2) ($\varepsilon \times 10^{-3}$) 249 (46.9), 289 (25.8), 416 (219), 533 (14.7), 569 (19.3); δ_H (400 MHz, $CDCl_3$) 0.96, 0.98 (2 t, *J* 7.6 Hz, $CH_2CH_2CH_2CH_3$); 1.50–1.61 (m, $CH_2CH_2CH_2CH_3$); 1.93–2.02 (m, $CH_2CH_2CH_2CH_3$); 2.66, 2.68 (2 s, β-pyrrolic CH_3); 3.59–3.74 (m, $CH_2CH_2CH_2CH_3$); 6.20, 6.28 (2 dd, 2H, *J* 3.6, 1.0 Hz, H 3′); 6.41 (d, *J* 3.9 Hz, thiophene H); 6.50–6.57 (m, thiophene H); 6.86 (dd, *J* 5.0, 1.0 Hz, H 5′); 6.98–7.02 (m, thiophene H); 7.13–7.28 (m, thiophene H); 7.30, 7.49 (2 s, H 4‴); 10.46, 10.47 (2 s, H 10 and 20); *m/z* (FAB-LRMS) cluster at 1464–1472, 1466 (80, M^+); *m/z* (FAB-HRMS) Found: 1466.2317 (M^+, $C_{80}H_{72}N_4Ni_1S_{10}$ requires 1466.2318).

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