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5,10,15,20-Tetrakis(N-protected-imidazol-2-yl)porphyrins.

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Abstract: it is shown that examples of the title porphyrins can be prepared from suitably N-protected imidazole-2-carboxaldehydes and pyrrole in refluxing propionic acid: subsequent deprotection, affords a synthetic route to 5,10,15,20-tetrakis(substituted-imidazol-2-yl)porphyrins (TIPs).

We recently reported the synthesis and characterisation of 5,10,15,20-tetrakis(imidazol-2-yl)porphyrin (TIP, **1c**, Scheme 1), and showed it to be a hydration-dependent proton conductor.[1] TIP, its imidazol-4-yl isomer,[2] and a 5,15-bis(imidazol-2-yl)-ß-octaalkylporphyrin[3] are, to our knowledge, the only imidazole-substituted porphyrins to be prepared. A recent paper reports attempts to synthesise imidazol-2-yl-substituted porphyrins via N-protected imidazole-2-carboxaldehydes, but without success.[4]

Our interest in imidazol-2-yl-substituted porphyrins stems from their proton-conducting properties, which we reasoned were due to hydrogen-bonded stacking interactions between porphyrin monomers.[1] It may in future be possible to utilise this effect to construct novel molecular electronic devices[5] using stacks of proton- and electron-conducting porphyrins based on TIPs. At the moment, however, it is unclear exactly how TIP monomers stack themselves in the solid state - whether imidazole moieties on one TIP monomer hydrogen bond to similar groups on neighbouring TIP monomers, or to the latters' central N-H's. The answer to this question has been elusive due in no small part to TIP's relative insolubility and intractability, thus making the preparation of crystalline samples for X-ray analysis virtually impossible.

To progress further with this work, a higher-yielding, more general synthesis is required in order to provide more tractable TIPs with solublising groups. TIP itself has only been obtained (via the Adler procedure)[6] in yields of $< 7\%$.[1] All attempts to prepare TIPs containing 4,5-di-substituted imidazole moieties via this methodology have failed. We have found, however, that a range of TIPs may be prepared in better yield if the imidazole groups are N-protected prior to porphyrin synthesis. In this paper, therefore, we report the synthesis of *meso*tetrakis(N-protected imidazol-2-yl)porphyrins, and their subsequent deprotection to give TIPs.

RESULTS AND DISCUSSION

The imidazole 1-N nitrogen can be blocked by a variety of N-protecting groups.[7] Formylation at the C-2 imidazole carbon is then achieved by generating the carbanion, via treatment with *n*-butyllithium or lithium isopropylamide, followed by reaction with DMF, and hydrolysis with water.[8] This procedure rules out the trichloroethoxycarbonyl and *o*-nitrobenzyl N-protecting groups: the former is unstable under the conditions necessary for carbanion generation, while the latter deactivates the imidazole 2-position to formylation.

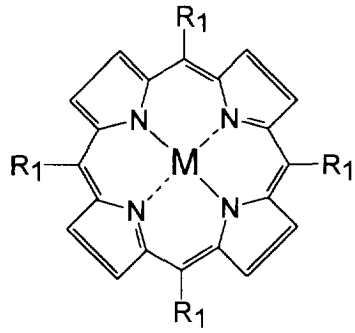
Whether the N-protected imidazole-2-carboxaldehyde so generated can be used to form a porphyrin depends to some extent on the steric bulk of the protecting group and whether that group can survive the reaction conditions necessary for porphyrin formation (i.e., for the Adler synthesis,[6] refluxing propionic acid). This rules out the trityl and the dimethylsulphamoyl N-protecting groups as they are removed under Adler conditions, while Lindsay porphyrin synthesis conditions[9] (dry DCM, $BF_3.Et_2O$, -30°C) gave no porphyrin and permitted recovery of the starting N-protected imidazole-2-carboxaldehydes.

The N-protecting group also has to be removable under mild conditions that do not affect the porphyrin. This rules out the allyl moiety as an imidazole N-protecting group because in order to remove it, the allyl group has first to be isomerised to a propenyl moiety[10] which is then oxidised away with $KMnO_4$ solution. We found that although 5,10,15,20-tetrakis(1-propenyl imidazol-2-yl)porphyrin could be formed, the conditions for its oxidative deprotection destroyed the porphyrin macrocycle.[11] We are currently examining alternative oxidative conditions that leave this porphyrin's macrocycle intact.

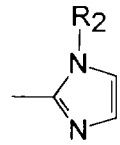
The two most convenient imidazole N-protecting groups turned out to be the benzyl (Bz) and *p*-methoxybenzyl (PMBz) moieties. These permitted porphyrin formation and were relatively easy to remove - the Bz group by catalytic transfer hydrogenation (CTH - with Pd black and 4.4% formic acid/methanol under N_2),[12] and the PMBz group with refluxing 6M HCl.[7] Removal of the Bz group was initially problematic in that catalytic transfer hydrogenation simultaneously reduces the porphyrin macrocycle to the chlorin and bacteriochlorin of the TIP. In the case of **1a** after CTH, this is seen in the uv/visible spectrum by the appearance of a band at 661 nm (due to the chlorin) and one at 760 nm (due to the bacteriochlorin). Reoxidation with the high-potential quinone DDQ was only partially successful, in that the band at 760 nm disappeared, but the band at 661 nm increased slightly in intensity. Clearly, 5,10,15,20-tetrakis(imidazol-2-yl)chlorin (TIC) is more resistant to oxidation than other *meso*-substituted chlorins, which are usually oxidised to porphyrins by DDQ.[13]

We reasoned that the four electron-withdrawing *meso*-imidazol-2-yl substituents were probably responsible for TIC's increased stability. If so, then this could be overcome by insertion of a metal cation that would increase electron density over the macrocycle, e.g., by d-pi* backbonding,[14] yet could itself be relatively easy to remove.[15] Such a metal cation is Ni(II). Indeed, insertion of Ni(II) into **1a**, followed by CTH gave a mixture of Ni(II)TIP, **1c**, and Ni(II)TIC, the latter now being readily reoxidised to Ni(II)TIP with DDQ in refluxing ethanol. Ultimately, the PMBz imidazole N-protecting group is less problematic in terms of its ease of removal, prior metallation of the porphyrin being unnecessary.

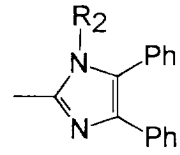
*Meso*tetrakis(N-protected imidazol-2-yl)porphyrins exhibit the phenomenon of atropoisomerism,[16] a feature typical of *meso*-(2-substituted-aryl)porphyrins. This is due to a high rotational energy barrier about



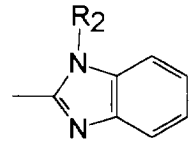
M = 2H or Ni(II)

1. R_1 = 

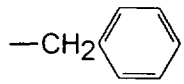
a; R_2 = Bz: **b;** R_2 = PMBz: **c;** R_2 = H.

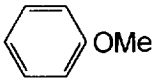
2. R_1 = 

a; R_2 = Bz: **b;** R_2 = PMBz: **c;** R_2 = H.

3. R_1 = 

a; R_2 = Bz: **b;** R_2 = PMBz:

Bz = 

PMBz = 

Scheme 1

the C-C bond joining the porphyrin *meso*- and imidazole 2-carbons, caused by steric hindrance between the imidazole N-benzyl protecting group and the porphyrin ß-hydrogens. Four atropoisomers are possible, (see Scheme 2) but in the N-protected (imidazol-2-yl)porphyrins reported here, only three were separated by column chromatography. In the case of **1a**, tlc indicates that after separation, each atropoisomeric fraction, on standing at ambient temperature becomes a mixture of all atropoisomers. For PMBz-protected TIP, **1b**, atropoisomer interconversion begins between 30-40°C, making atropoisomer separation a clear possibility.

Atropoisomerism in these compounds is further demonstrated in the ^{1}H-nmr spectra which show complex resonances for the porphyrin central N-H and ß-protons that in non-atropoisomeric porphyrins are simple. Previous work has shown that these anomalies may be explained in terms of steric and electronic interactions between the porphyrin macrocycle and the bulky, electron-withdrawing *meso*-substituents, in this case, N-protected imidazol-2-yl groups.[17] This generates distortions of the porphyrin and a decrease in macrocyclic ring current which, in turn, leads to non-uniform perturbations of chemical shifts throughout the molecule. Instead of a simple ^{1}H-nmr spectrum, therefore, non-equivalent resonances are observed for an otherwise symmetrically substituted porphyrin.

Support for this idea in this work interestingly, comes from the ^{1}H-nmr spectrum of the Ni(II) complex of **1a**, which shows moderate line-broadening due to the presence of a paramagnetic centre in the molecule (the compound was purified several times to ensure the absence of any paramagnetic impurities). *Meso*-substituted nickel(II) porphyrins generally have a square planar geometry that confers diamagnetism on the d^8 metal cation.[18] Nickel (II) porphyrins become paramagnetic when ligands (e.g., pyridine) bind to the metal cation 5th and 6th positions, due to the metal cation having roughly octahedral geometry.[19] This could conceivably occur if the imidazole nitrogen of one metalloporphyrin monomer coordinated to the metal cation of another. Though this is unlikely (as the bulky N-benzyl protecting groups should hinder close approach of two monomers), there is evidence from uv/visible spectroscopy that some aggregation between monomers is occurring. However, the deprotected metalloporphyrin, Ni(II)TIP **1c** (in which such coordination would be more likely), is diamagnetic, indicating that the central Ni(II) cation is in a square-planar geometry with no 5th and 6th ligands.

A more plausible reason for the paramagnetism of the Ni(II) complex of **1a** is that distortion of the macrocycle by the bulky *meso*-substituents produces a roughly tetrahedral geometry about the Ni(II) cation, and the Ni(II) cation with tetrahedral geometry is known to be paramagnetic.[20]

Thus, with suitably N-protected imidazole-2-carboxaldehydes, it should be possible to prepare *meso*(imidazol-2-yl)porphyrins with solublising substituents in the imidazole 4- and/or 5-positions that would allow easier manipulation of the porphyrin than **1c**. We prepared therefore, N-benzyl and N-PMB-protected *meso*tetrakis(4,5-diphenylimidazol-2-yl)porphyrin, i.e., **2a** and **2b**, first by N-protection of 4,5-diphenyl imidazole, followed by formylation, then porphyrin synthesis by refluxing the N-protected imidazole-2-carboxaldehyde with pyrrole in propionic acid. Finally, deprotection afforded the porphyrin **2c**.

In the case of **2a**, deprotection was achieved, as previously stated, by prior nickel (II) insertion into the protected porphyrin. Unlike the Ni(II) complex of **1a**, however, the nickel(II) complex of **2a** was **not** paramagnetic (as demonstrated by ^{1}H-nmr), suggesting that the porphyrin macrocycle is under less steric pressure to distort tetrahedrally about the Ni(II) metal cation. This seems surprising given that 1-benzyl-4,5-

α means imidazole N-protecting group points up; β down

Diagramatic representation of atropoisomers

Scheme 2

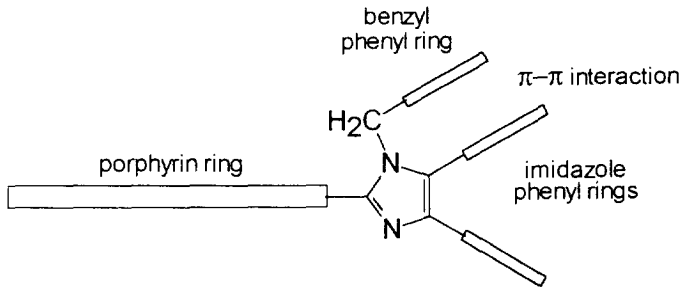


Diagram showing π–π interaction between benzyl and imidazole phenyl rings in **2a**

Scheme 3

diphenylimidazole groups are larger than 1-benzylimidazole moieties. Molecular models, however, show that (scheme 3) the phenyl ring of the 1-benzyl group may be less sterically hindering because it can lie parallel to the imidazole 5-phenyl group and could be held in such a position by pi-pi interactions between the two rings.[21] Such an interaction is not possible for the 1-benzylimidazole substituent.

We have also prepared N-protected *meso*tetrakis(benzimidazol-2-yl)porphyrins, **3a** and **3b**, and preliminary results indicate that they too may be deprotected to the porphyrin **3c**. Interestingly, as with **2a**, the Ni(II) complex of **3a** was not paramagnetic (as demonstrated by ^{1}H-nmr), indicating less steric pressure on the macrocycle. Again, molecular models show that this pressure could be alleviated by a pi-pi interaction between the 1-benzyl protecting group's phenyl ring, and the fused benzene ring on the imidazole moieties.

Finally, there is evidence from the uv/visible spectra of these porphyrins, of aggregation in solution.[22] Thus, the B bands of the Ni(II) complexes **1a** and **3a** are narrower, red-shifted, and of increased intensity on addition of pyridine. The uv/visible spectra of the free-base porphyrins **1a** and **3a** are, in contrast, little affected by pyridine addition. We also observed that the B band uv/visible spectra of **2c** were exceptionally broadened and red-shifted for the free-base and the Ni(II) complex. These data could indicate that aggregation is enhanced for these compounds, regardless of whether they were protected or not. Such observations bode well for the possible stacking of these porphyrins in the solid state, and their subsequent molecular conducting properties. We shall be reporting on these elsewhere.

CONCLUSIONS

We have shown that, contrary to an earlier report, it is possible to prepare porphyrins with N-protected imidazol-2-yl *meso*-substituents and that in certain cases these compounds can be deprotected to afford *meso*tetrakis(imidazol-2-yl)porphyrins. It should now be possible to prepare a range of these compounds and measure their proton- and/or electron-conducting properties.

EXPERIMENTAL

Uv/visible spectra were recorded on a Cecil CF 5500 double beam instrument or a Hewlett-Packard HP 8453 Diode-Array spectrometer, using spectroscopic grade chloroform or dichloromethane as solvent. Infra-red spectra were recorded as KBr discs or as thin films between NaCl plates using a Perkin-Elmer 1420 Ratio Recording Infra-red spectrometer. Proton nmr spectra were recorded on a Varian CFT-20 or a Jeol JNM FX 200 spectrometer using $CDCl_3$ as sovent and TMS as internal reference. Mass spectra were recorded on an AEI MS902 spectrometer. FABS mass spectra and accurate mass measurements (reference standard polyethylene glycol) were recorded by the EPSRC's Mass Spectroscopy Sevice at Swansea. Microanalyses were performed by MEDAC Ltd at Brunel University on a Carlo Erba 1106 elemental analyser or a Control Equipment Corporation Model 240XA. Tlc was performed on aluminium-backed silica-gel 60 F_{254} and/or neutral alumina 60 F_{254} type E plates. Porphyrins were separated by column chromatography on neutral alumina (Brockmann grade 3, 150 mesh). All chromatography materials, solvents, and reagents were supplied by Aldrich and used as supplied unless otherwise stated.

Synthesis of N-Protected Imidazoles

1-Benzylimidazole - This was obtained from Aldrich or synthesised by a literature method.[10b] The desired product (1.02 g, 22%) as a white solid, m.p. = 67 - 69°C. MS(E.I.): found m/z = 158 (M^+, 100%), requires m/z = 158. δ_H (ppm): 7.48 (s, 1H, imidazole-C2-H), 7.1-7.4 (m, 5H, phenyl-H), 7.03 (s, 1H, imidazole-C4-H), 6.84 (s, 1H, imidazole-C5-H), 5.06 (s, 2H, benzyl-CH_2).

1-p-Methoxybenzylimidazole - To a stirred mixture of imidazole (1.5 g, 0.022 mol) and excess K_2CO_3 (1.68 g) in dry DMF (29 mL) at 80°C under N_2 was slowly added *p*-methoxybenzyl chloride (3.5 g, 0.022 mol). The reaction was allowed to cool to room temperature, filtered and evaporated under vacuum to an oil. This was purified by column chromatography (eluting with ethyl acetate) and the combined eluants evaporated to give an off-white solid of the desired N-protected imidazole (2.15 g, 52%), m.p. = 57-60°C (Found: C, 69.6; H, 6.4; N, 14.6. $C_{11}H_{12}N_2O.^1/_8H_2O$ requires C, 69.35; H, 6.56; N, 14.88%). MS(E.I.) m/z = 188 (M^+, 38%), requires m/z = 188. δ_H(ppm): 7.45 (s, 1H, imidazole-C2-H), 7.02, 7.00, 6.84, 6.82 (q, 4H, *p*-methoxyphenyl-H AB spin system, J_{AB} = 8.54Hz), 6.87 (s, 1H, imidazole-C4-H), 6.76 (s, 1H, imidazole-C5-H), 5.00 (s, 2H, benzyl-CH_2), 3.77 (phenyl-OCH_3). IR(KBr) cm^{-1}: 3094 (w, aromatic-CH stretch), 2998-2800 (w, aliphatic-CH stretch), 1612, 1598, 1512, 1456 (m, C=C, C=N ring stretch), 1248 (s, ether C-O-C asymmetric stretch), 1026 (m, ether symmetric stretch), 829, 740 (m, C=C-H out-of-plane bend), 690 (w, C=C out-of-plane bend).

1-Benzyl-4,5-diphenylimidazole - This N-protected imidazole was synthesised from 4,5-diphenylimidazole (15.00 g, 0.068 mol), excess potassium carbonate (5.40 g), and benzyl chloride (8.60 g, 0.068 mol) in dry DMF (200 mL) by the same protocol as for 1-benzylimidazole. Removal of the solvent gave a solid residue which, on trituration afforded the desired product (18.40 g, 90%) as a white solid, m.p. = 113-115°C (Found: C, 84.5; H, 5.9; N, 8.7. $C_{22}H_{18}N_2.^1/_6H_2O$ requires C, 84.35; H, 5.86; N, 8.96%). MS(E.I.): found m/z = 310 (M^+, 80%); requires m/z = 310. δ_H (ppm): 7.64 (1s, 1H, imidazole-C2-H), 6.95-7.5 (m, 15H, phenyl-H), 4.96 (s, 2H, benzyl-CH_2). IR (KBr disc) cm^{-1}: 3120-3010 (w, aromatic-CH stretch), 2980-2890 (w, aliphatic-CH stretch), 1600, 1499, 1438, 1353 (m, C=C, C=N ring stretch), 1111, 1063, 1019 (m, aromatic-CH in-plane bend), 788, 763, 715, 700 (s, C=C-H out-of-plane bend), 650 (s, C=C out-of-plane bend).

1-p-Methoxybenzyl-4,5-diphenylimidazole - This N-protected imidazole was synthesised from 4,5-diphenylimidazole (1.55 g, 7.04 mmol), excess potassium carbonate (0.56 g), and *p*-methoxybenzyl chloride (1.10 g, 7.04 mmol) in dry DMF (25 mL) by the same protocol as for 1-*p*-methoxybenzylimidazole. Removal of the solvent gave an oil which, after purification by column chromatography on silica gel (eluting with 70% ethyl acetate/petroleum ether 40:60) afforded the desired product (2.06 g, 86%) as a white solid, m.p. = 87-90°C (Found: C, 80.8; H, 5.8; N, 8.1. $C_{23}H_{20}N_2O.^1/_8H_2O$ requires C, 80.64; H, 5.92; N, 8.18%). MS(E.I.): found m/z = 340 (M^+, 15%); requires m/z = 340. δ_H (ppm): 7.60 (1s, 1H, imidazole-C2-H), 7.10-7.51 (m, 10H, phenyl-H), 6.92, 6.88, 6.81, 6.77 (q, 4H, *p*-methoxyphenyl-H AB spin-system, J_{AB} = 9.27Hz), 4.88 (s, 2H, *p*-methoxybenzyl-CH_2), 3.77 (*p*-methoxybenzyl-OCH_3). IR (KBr) cm^{-1}: 3108-3000 (w, aromatic-CH stretch), 2920-2825 (w, aliphatic-CH stretch), 1610, 1512, 1448 (s, C=C, C=N ring

stretch), 1252 (s, ether, C-O-C asymmetric stretch), 1024 (m, ether C-O-C symmetric stretch), 825, 813, 765 (s, C=C-H out-of-plane bend), 650 (s, C=C-H out-of-plane bend).

1-Benzylbenzimidazole - This N-protected imidazole was synthesised from benzimidazole (2.12 g, 0.018 mol), excess potassium carbonate (1.46 g), and benzyl chloride (2.50 g, 0.02 mol) in dry DMF (50 mL) by the same protocol as before. Removal of the solvent gave a viscous brown oil which, after column chromatography on silica gel (eluting with ethyl acetate), followed by crystallisation of the eluant with 40/60 petroleum ether gave a light-brown solid (2.33 g, 62%) as needle-like crystals, m.p. = 116-118°C (Found: C, 79.8; H, 5.8; N, 13.3. $C_{14}H_{12}N_2.{}^1/_6H_2O$ requires C, 79.58; H, 5.89; N, 13.27%). MS(E.I.): found m/z = 208 (M^+, 54%); requires m/z = 208. δ_H (ppm): 8.07 (1s, 1H, benzimidazole-C2-H), 7.14-7.85 (m, 9H, phenyl-H and fused benzene-H), 5.33 (s, 2H, benzyl-CH_2). IR (KBr disc) cm^{-1}: 3105-3010 (w, aromatic-CH stretch), 2940 (w, aliphatic-CH stretch), 1610, 1500, 1452 (m, C=C, C=N ring stretch), 1180, 1080, 1005 (m, aromatic-CH in-plane bend), 756, 723 (s, C=C-H out-of-plane bend), 697 (s, C=C out-of-plane bend).

1-p-Methoxybenzylbenzimidazole - This N-protected imidazole was synthesised from benzimidazole (3.54 g, 0.03 mol), excess potassium carbonate (2.4 g), and *p*-methoxybenzyl chloride (4.7 g, 0.03 mmol) in dry DMF (909 mL) by the same protocol as for 1-*p*-methoxybenzylimidazole. Removal of the solvent gave an oil which, after purification by column chromatography on silica gel (eluting with ethyl acetate) afforded the desired product (5.11 g, 72%) as an off-white solid, m.p. = 64-66°C (Found: C, 74.7; H, 5.8; N, 11.5. $C_{15}H_{14}N_2O.{}^1/_8H_2O$ requires C, 74.89; H, 5.97; N, 11.65%). MS(E.I.): found m/z = 238 (M^+, 95%); requires m/z = 238. δ_H (ppm): 7.92 (1s, 1H, benzimidazole-C2-H), 7.10-7.51 (m, 10H, phenyl-H), 7.84-7.23 (m, 4H, benzimidazole-H), 7.16, 7.12, 6.88, 6.84 (q, 4H, *p*-methoxyphenyl-H AB spin-system, J_{AB} = 8.79Hz), 5.29 (s, 2H, *p*-methoxybenzyl-CH_2), 3.79 (*p*-methoxybenzyl-OCH_3). IR (KBr) cm^{-1}: 3120-3010 (w, aromatic-CH stretch), 2998-2810 (w, aliphatic-CH stretch), 1610, 1510, 1458, 1410 (s, C=C, C=N ring stretch), 1248 (s, ether, C-O-C asymmetric stretch), 1028 (m, ether C-O-C symmetric stretch), 789, 738 (s, C=C-H out-of-plane bend).

Synthesis of N-Protected Imidazole-2-carboxaldehydes.

1-Benzylimidazole-2-carboxaldehyde - To a solution of 1-benzylimidazole (5.0 g, 0.032 mol) in dry THF (87 mL) at -40°C under N_2, was added *n*-butyllithium (19.71 mL of a 1.6M solution in hexanes). During addition, the temperature was not allowed to rise above -30°C. After addition of the *n*-butyllithium, the mixture was continued stirring during 15 min at -40°C, and then excess dry DMF (7 mL) was added, and the reaction continued stirring for a further 2 h. The reaction was then quenched with aqueous $NaHCO_3$ solution (70 mL), and the THF removed under vacuum. The remaining aqueous solution was then extracted with $CHCl_3$ (3*100 mL) and the combined extracts dried over $MgSO_4$, filtered and concentrated to give an oily residue. This was then purified by column chromatography on silica gel (eluting with ethyl acetate), the combined eluants being evaporated to afford the desired N-protected imidazole-2-carboxaldehyde (4.16 g, 71%) as a colourless viscous oil (Found: C, 70.6; H, 5.4; N, 14.5. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.41; N, 15.04%). MS(E.I.) m/z = 186 (M^+, 38%), requires m/z = 186. δ_H (ppm): 9.85 (s, 1H, -CHO), 7.14-7.38 (m, 7H, phenyl-H and imidazole-H), 5.62 (s, 2H, benzyl-CH_2). IR(NaCl) cm^{-1}: 3160-3010 (w, aromatic C-H stretch), 2840 (w, aliphatic C-H stretch), 1680 (s, aldehyde C=O stretch), 1495, 1470, 1452

(m, C=C, C=N ring stretch), 1160, 1070, 1020 (m, aromatic C-H in-plane bend), 770, 710 (s, C=C-H out-of-plane bend), 690 (m, C=C, out-of-plane bend).

1-p-Methoxybenzylimidazole-2-carboxaldehyde - A dry THF (30 mL) solution of 1-*p*-methoxybenzylimidazole (2.07 g, 0.011 mol) was reacted with *n*-butyllithium (6.9 mL of a 1.6M solution in hexanes) using the same protocol as the previous 1-benzylimidazole-2-carboxaldehyde, to afford the N-protected imidazole-2-carboxaldehyde as a colourless oil (1.96 g, 82%). (Found: C, 66.1; H, 5.7; N, 12.6. $C_{12}H_{12}N_2O_2.{}^1/_8H_2O$ requires C, 66.18; H, 5.67; N, 12.83%). MS(E.I.) m/z = 216 (M^+, 91%), requires m/z = 216. δ_H (ppm): 9.85 (s, 1H, -CHO), 7.27 (s, 1H, imidazole-H), 7.11 (s, 1H, imidazole-H), 7.19, 7.17, 6.88, 6.86 (q, 4H, *p*-methoxyphenyl-H, AB spin-system, J_{AB} = 8.60 Hz), 5.54 (s, 2H, *p*-methoxybenzyl-CH_2), 3.79 (s, 3H, *p*-methoxybenzyl-OCH_3). IR(NaCl) cm^{-1}: 3180-3010 (w, aromatic C-H stretch), 2980-2815 (w, aliphatic C-H stretch), 1698 (s, aldehyde C=O stretch), 1620, 1598, 1515,1477, (m, C=C, C=N ring stretch), 1260 (m, ether C-O-C asymmetric stretch), 1087, 1070 (m, aromatic C-H in-plane bend), 1040 (m, ether C-O-C symmetric stretch), 826, 775 (s, C=C-H out-of-plane bend), 690 (w, C=C out-of-plane bend).

1-Benzyl-4,5-diphenylimidazole-2-carboxaldehyde - A dry THF (150 mL) solution of 1-benzyl-4,5-diphenylimidazole (18.00 g, 0.06 mol) was reacted with *n*-butyllithium (38 mL of a 1.6M solution in hexanes) using the same protocol as above to give a solid residue which, on trituration with diethyl ether afforded the N-protected imidazole-2-carboxaldehyde (15.11 g, 76%) as a white solid, m.p. = 154-156°C (Found: C, 81.5; H, 5.3; N, 8.3. $C_{23}H_{18}N_2O$ requires C, 81.63; H, 5.36; N, 8.28%). MS(E.I.) m/z = 338 (M^+, 96%), requires m/z = 338. δ_H (ppm): 9.94 (s, 1H, -CHO), 7.80-7.60 (m, 15H, combined phenyl- and imidazole aromatic-H), 5.53 (s, 2H, benzyl-CH_2). IR(KBr) cm^{-1}: 3100-3028 (w, aromatic C-H stretch), 2958, 2850 (w, aliphatic C-H stretch), 1674 (s, aldehyde C=O stretch), 1602, 1500, 1448, 1412 (m, C=C, C=N ring stretch), 1140, 1074, 1028 (m, aromatic C-H in-plane bend), 830, 794, 728, 702 (s, C=C out-of-plane bend).

1-p-Methoxybenzyl-4,5-diphenylimidazole-2-carboxaldehyde - A dry THF (35 mL) solution of 1-*p*-methoxybenzyl-4,5-diphenylimidazole (2.00 g, 5.88 mmol) was reacted with *n*-butyllithium (3.68 mL of a 1.6M solution in hexanes) using the same protocol as the previous 1-benzylimidazole-2-carboxaldehyde, to afford the N-protected imidazole-2-carboxaldehyde as a waxy solid which on recrystallisation from ethyl acetate and 40/60 petroleum ether, gave a white solid (0.94 g, 43%), m.p. = 131-133°C (Found: C, 78.2; H, 5.5; N, 7.6. $C_{24}H_{20}N_2O_2$ requires C, 78.24; H, 5.45; N, 7.60%). MS(E.I.) m/z = 368 (M^+, 71%), requires m/z = 368. δ_H (ppm): 9.34 (s, 1H, -CHO), 7.50-7.18 (m, 10H, phenyl-H), 6.81, 6.77, 6.75, 6.70 (q, 4H, *p*-methoxyphenyl-H, AB spin-system, J_{AB} = 9.15 Hz), 5.47 (s, 2H, *p*-methoxybenzyl-CH_2), 3.75 (s, 3H, *p*-methoxybenzyl-OCH_3). IR(KBr) cm^{-1}: 3064 (w, aromatic C-H stretch), 2956-2836 (w, aliphatic C-H stretch), 1678 (s, aldehyde C=O stretch), 1608, 1512, 1446, (m, C=C, C=N ring stretch), 1254 (m, ether C-O-C asymmetric stretch), 1022 (m, ether C-O-C symmetric stretch), 834, 774, 700 (s, C=C-H out-of-plane bend).

1-Benzylbenzimidazole-2-carboxaldehyde - A dry THF (50 mL) solution of 1-benzylbenzimidazole (2.13 g, 0.01 mol) was reacted with *n*-butyllithium (6.4 mL of a 1.6M solution in hexanes) using the same protocol as above to give a viscous oil which solidified on cooling to afford the N-protected imidazole-2-

carboxaldehyde (0.65 g, 27%) as a white solid, m.p. = 105-107°C (Found: C, 76.5; H, 5.2; N, 11.9. $C_{15}H_{12}N_2O$ requires C, 76.25; H, 5.12; N, 11.86%). MS(E.I.) m/z = 236 (M^+, 96%), requires m/z = 236. δ_H (ppm): 10.15 (s, 1H, -CHO), 7.97-7.16 (m, 9H, combined phenyl- and benzimidazole aromatic-H), 5.87 (s, 2H, benzyl-CH_2). IR(KBr) cm^{-1}: 3040-3029 (w, aromatic C-H stretch), 2988, 2872 (w, aliphatic C-H stretch), 1688 (s, aldehyde C=O stretch), 1608, 1464, 1450, 1412 (m, C=C, C=N ring stretch), 1160, 1072, 1022 (m, aromatic C-H in-plane bend), 774, 742, (m, C=C-H out-of-plane bend), 690 (m, C=C out-of-plane bend).

1-p-Methoxybenzylbenzimidazole-2-carboxaldehyde - A dry THF (100 mL) solution of 1-*p*-methoxybenzylbenzimidazole (5.00 g, 0.021 mol) was reacted with *n*-butyllithium (13.1 mL of a 1.6M solution in hexanes) using the same protocol as for 1-benzylimidazole-2-carboxaldehyde, to afford the N-protected imidazole-2-carboxaldehyde as an off-white solid (0.94 g, 43%), m.p. = 73-75°C (Found: C, 72.1; H, 5.3; N, 10.5. $C_{16}H_{14}N_2O_2$ requires C, 72.18; H, 5.26; N, 10.53%). MS(E.I.) m/z = 266 (M^+, 96%), requires m/z = 266. δ_H (ppm): 10.14 (s, 1H, -CHO), 7.95-7.37 (m, 4H, benzylimidazole-H), 7.16, 7.14, 6.82, 6.80 (q, 4H, *p*-methoxyphenyl-H, AB spin-system, J_{AB} = 8.65 Hz), 5.79 (s, 2H, *p*-methoxybenzyl-CH_2), 3.75 (s, 3H, *p*-methoxybenzyl-OCH_3). IR(KBr) cm^{-1}: 3120- 3010 (w, aromatic C-H stretch), 2998-2800 (w, aliphatic C-H stretch), 1698 (s, aldehyde C=O stretch), 1612, 1512, 1472, 1410 (m, C=C, C=N ring stretch), 1248 (m, ether C-O-C asymmetric stretch), 1028 (m, ether C-O-C symmetric stretch), 806, 790, 738 (s, C=C-H out-of-plane bend).

Synthesis of *Meso*tetrakis(N-protected imidazol-2-yl)porphyrins.

(Unless otherwise stated, ^{1}H-nmr spectra were of atropoisomeric mixtures and are not included).

Mesotetrakis(1-benzylimidazol-2-yl)porphyrin **1a** - To a stirred, refluxing solution of propionic acid (430 mL) was added 1-benzylimidazole-2-carboxaldehyde (4.0 g, 0.02 mol). Pyrrole (1.34 g, 0.02 mol) was then added and the reaction continued refluxing and stirring during 4 h. The propionic acid was then removed by distillation under reduced pressure to give a dark residue. This was taken into the minimum of $CHCl_3$ and subjected to column chromatography on alumina. Three separate red atropoisomeric fractions were eluted and, after concentration, crystallised with hexane (fraction 1; 0.28 g, 6%: fraction 2; 0.44 g, 9%: fraction 3; 0.41 g, 8%: total yield = 23%), m.p. >300°C. (Found: C, 75.8; H, 4.9; N, 17.4. $C_{60}H_{46}N_{12}.{}^3/_4H_2O$ requires C, 75.99; H, 5.01; N, 17.73%). FAB-MS m/z = 935 (M^++1) requires m/z = 935. λ_{max}($CHCl_3$)($\varepsilon/10^3$, 1 $mol^{-1}cm^{-1}$): 425 (328), 517 (32.9), 548 (sh), 593 (18.4), 661 (16.6). IR (KBr) cm^{-1}: 3326 (w, porphyrin N-H stretch), 3160-3020 (w, aromatic C-H stretch), 2940 (w, aliphatic C-H stretch), 1570, 1503, 1462, 1428, 1345 (m, aromatic C=C, C=N ring stretch), 1128, 1085, 1012 (m, aromatic C-H in-plane bend), 1060 (w, porphyrin C-H in-plane bend), 978 (m, porphyrin macrocycle bend), 812, 740, 715 (s, aromatic C=C-H out-of-plane bend).

Mesotetrakis(1-p-methoxybenzylimidazol-2-yl)porphyrin **1b** - To a stirred, refluxing solution of propionic acid (100 mL) was added 1-*p-methoxy*benzylimidazole-2-carboxaldehyde (0.63 g, 2.9 mmol). Pyrrole (0.20 g, 3.0 mmol) was then added and the reaction continued refluxing and stirring during 4 h. The propionic acid was then removed by distillation under reduced pressure to give a dark residue. This was

taken into the minimum of $CHCl_3$ and subjected to column chromatography on alumina. Three separate red atropoisomeric fractions were eluted and, after concentration, crystallised with hexane to give deep purple microcrystals (total yield of all fractions = 0.160 g, 21%), m.p. >300°C. (Found: C, 69.2; H, 5.2; N, 14.9. $C_{64}H_{54}N_{12}O_4.3H_2O$ requires C, 69.28; H, 5.16; N, 14.93%). FAB-MS m/z = 1055 ($M^+ + 1$) requires m/z = 1055. $\lambda_{max}(CHCl_3)$($\varepsilon/10^3$, l $mol^{-1}cm^{-1}$): 425 (108), 516 (10.9), 544 (sh), 589 (4.4), 662 (4.4). IR (KBr) cm^{-1}: 3314 (w, porphyrin N-H stretch), 3180-3010 (w, aromatic C-H stretch), 2934, 2863 (w, aliphatic C-H stretch), 1610, 1512, 1460, 1338 (m, aromatic C=C, C=N ring stretch), 1248 (s, ether C-O-C asymmetric stretch), 1176, 1118 (m, aromatic C-H in-plane bend), 1030 (m, ether C-O-C symmetric stretch), 970 (m, porphyrin macrocycle bend), 806, 760, 742 (s, aromatic C=C-H out-of-plane bend).

Mesotetrakis(1-benzyl-4,5-diphenylimidazol-2-yl)porphyrin **2a** - To a stirred, refluxing solution of propionic acid (500 mL) was added 1-benzyl-4,5-diphenylimidazole-2-carboxaldehyde (15.00 g, 0.044 mol). Pyrrole (2.95 g, 0.044 mol) was then added and the reaction continued refluxing and stirring during 4 h. The propionic acid was then removed by distillation under reduced pressure to give a dark residue. This was taken into the minimum of $CHCl_3$ and subjected to column chromatography on alumina. Three separate red atropoisomeric fractions were eluted and, after concentration, crystallised with hexane (total yield = 3.42 g, 20%). Identification and characterisation of all three fractions proved them to be the same compound. The first fraction was isolated as a single isomer, m.p. >300°C. (Found: C, 83.1; H, 5.0; N, 10.8. $C_{108}H_{78}N_{12}.{}^2/_3H_2O$ requires C, 83.36; H, 5.14; N, 10.81%). FAB-MS (3-NOBA, dichloromethane) m/z = 1544 (M^+) requires m/z = 1544. $\lambda_{max}(CHCl_3)$($\varepsilon/10^3$, l $mol^{-1}cm^{-1}$): 445 (171), 528 (13.7), 570 (6.3), 596 (4.5), 668 (2.3). λ_{max}(methanolic HCl): 499, 619, 686. δ_{ppm}: 9.16 (s, 2H, ß-H), 7.97-5.90 (m, 60H, aromatic protons), 4.87 (s, 8H, benzyl-CH_2), -2.70 (s, 2H, porphyrin N-H). IR (KBr) cm^{-1}: 3318 (w, porphyrin N-H stretch), 3083-3028 (w, aromatic C-H stretch), 2925 (w, aliphatic C-H stretch), 1602, 1496, 1478, 1398 (m, aromatic C=C, C=N ring stretch), 1108, 1072, 1028 (m, aromatic C-H in-plane bend), 962 (m, porphyrin macrocycle bend), 800, 774, 728, 696 (s, aromatic C=C-H out-of-plane bend).

Mesotetrakis(1-p-methoxybenzyl-4,5-diphenylimidazol-2-yl)porphyrin **2b** - To a stirred, refluxing solution of propionic acid (60 mL) was added 1-*p-methoxy*benzyl-4,5-diphenylimidazole-2-carboxaldehyde (0.94 g, 2.55 mmol). Pyrrole (0.17 g, 2.55 mmol) was then added and the reaction continued refluxing and stirring during 4 h. The propionic acid was then removed by distillation under reduced pressure to give a dark residue. This was taken into the minimum of $CHCl_3$ and subjected to column chromatography on alumina. Three separate chemically identical red atropoisomeric fractions were eluted and, after concentration, crystallised with hexane to give purple/brown amorphous solids (total yield of all fractions = 0.32 g, 30%), m.p. >300°C. (Found: C, 78.1; H, 5.1; N, 9.8. $C_{112}H_{86}N_{12}O_4.3H_2O$ requires C, 78.29; H, 5.40; N, 9.78%). FAB-MS (3-NOBA, chloroform) m/z = 1665 ($M^+ + 1$) requires m/z = 1665. $\lambda_{max}(CHCl_3)$ ($\varepsilon/10^3$, l $mol^{-1}cm^{-1}$): 444 (131), 528 (15.9), 572 (8.1), 596 (8.3), 672 (3.7). $\lambda_{max}(CHCl_3$ + TFA) ($\varepsilon/10^3$, l $mol^{-1}cm^{-1}$): 508 (147), 622 (46.7), 702 (72.6). IR (KBr) cm^{-1}: 3305 (w, porphyrin N-H stretch), 3058-3000 (w, aromatic C-H stretch), 2930, 2822 (w, aliphatic C-H stretch), 1610, 1512, 1446, 1396 (m, aromatic C=C, C=N ring stretch), 1250 (s, ether C-O-C asymmetric stretch), 1032 (m, ether C-O-C symmetric stretch), 964 (m, porphyrin macrocycle bend), 782, 776, 698 (s, aromatic C=C-H out-of-plane bend).

Mesotetrakis(1-benzylbenzimidazol-2-yl)porphyrin **3a** - To a stirred, refluxing solution of propionic acid (50 mL) was added 1-benzylbenzimidazole-2-carboxaldehyde (0.60 g, 2.54 mmol). Pyrrole (0.17 g, 2.54 mmol) was then added and the reaction continued refluxing and stirring during 4 h. The propionic acid was then removed by distillation under reduced pressure to give a deep red tar. This was taken into the minimum of $CHCl_3$ and subjected to column chromatography on alumina. The atropoisomers did not separate cleanly but gave only two fractions which were eluted with DCM and crystallised with hexane as purple amorphous solids (fraction 1; 0.055 g, 8%: fraction 2; 0.062 g, 9%: total yield = 17%), m.p. >300°C. (Found: C, 79.4; H, 4.7; N, 14.3. $C_{76}H_{54}N_{12}.H_2O$ requires C, 79.13; H, 4.90; N, 14.58%). FAB-MS (3-NOBA, DCM) m/z = 1136 ($M^+ +1$) requires m/z = 1136. $\lambda_{max}(CHCl_3)(\varepsilon/10^3, l\ mol^{-1}cm^{-1})$: 430 (227), 517 (20.6), 549 (sh), 593 (18.4), 665 (5.0). IR (KBr) cm^{-1}: 3307 (w, porphyrin N-H stretch), 3180-3033 (w, aromatic C-H stretch), 1608, 1496, 1448, 1390, 1332 (m, aromatic C=C, C=N ring stretch), 1154 (w, porphyrin C-H in-plane bend), 1075, 1036 (m, aromatic C-H in-plane bend), 964 (m, porphyrin macrocyclic C-H in-plane bend), 800, 730, (s, aromatic C=C-H out-of-plane bend), 694 (m, aromatic C=C out-of-plane bend).

Formation of Deprotected TIPs

Mesotetrakis(imidazol-2-yl)porphyrinatonickel(II) **Ni(II)1c** - A mixture of **1a** (0.70 g, 0.75 mmol) and excess nickel(II) acetate (0.40 g) in glacial acetic acid (100 mL) was refluxed during 30 min. The acetic acid was removed by vacuum distillation to give a violet-black residue which was subjected to column chromatography on alumina (eluting with 3% methanolic chloroform). The three atropoisomers co-chromatographed as one band, which on crystallisation with ether afforded the Ni(II) complex of **1a** (0.27 g, 36%). This complex (0.14 g, 0.14 mmol), together with palladium black (0.54 g) were strirred together at room temperature in 4.4% formic acid in methanol, under N_2 during 24 h. The solution was filtered, and evaporated to dryness to give a purple solid consisting of a mixture of Ni(II)**1c** (i.e., Ni(II)TIP) and the metallochlorin, Ni(II)TIC. This solid was dissolved in ethanol (40 mL) to give a blue-green solution, excess of the high-potential quinone DDQ (0.50 g) added, and the mixture refluxed during 24 h. The solution was evaporated to dryness, and the resulting solid triturated with acetone. Filtration afforded a deep purple solid of Ni(II)TIP (0.069 g, 80%), m.p. >300°C (Found: C, 57.8; H, 3.4; N, 25.2. $C_{32}H_{20}N_{12}Ni.^3/_2H_2O$ requires C, 58.15; H, 3.51; N, 25.45.) FAB-MS (3-NOBA, TFA): m/z = 631 ($M^+ +1$), requires m/z = 631. λ_{max}(3M HCl) ($\varepsilon/10^3$, $l\ mol^{-1}cm^{-1}$): 420(224), 548 (15.3), 579 (7.0). δ_{ppm}(*d*-TFA): 9.08 (s, 8H, ß-H), 8.20 (s, 8H, imidazole-C-H). IR (KBr) cm^{-1}: 3500-2500 (s, broad, H-bonded N-H stretch), 1562, 1538, 1424, 1328 (m, imidazole and porphyrin C=C, C=N in-plane bend), 1288, 1102 (m, imidazole C-H in-plane bend), 994 (m, porphyrin macrocylic bend), 832, 790, 756, 708 (m, aromatic C-H out-of-plane bend).

Mesotetrakis(imidazol-2-yl)porphyrin **1c** - A solution of **1b** (0.03 g, 0.028 mmol) in 6M HCl (50 mL) was refluxed during 24 h and then allowed to cool to room temperature. The solution was evaporated to dryness under reduced pressure and the solid residue stirred in a solution DCM containing 4% triethylamine. The solid was filtered and washed with DCM to afford the desired deprotected porphyrin **1c** (0.016 g, 96%), which was identical to previously prepared samples of TIP.[1] M.p. >300°C. FAB-MS (3-NOBA, TFA) m/z = 575 ($M^+ +1$), requires m/z = 575. λ_{max}(0.01M HCl) ($\varepsilon/10^3$, $l\ mol^{-1}cm^{-1}$): 412 (112), 511 (12.5), 582

(5.4), 633 (1.7), 661 (1.2). λ_{max}(12M HCl): 465 (134), 605 (8.9), 662 (23.8). δ_{ppm}(*d*-TFA): 9.10 (s, 8H, ß-H), 8.53 (s, 8H, imidazole-C-H).

Mesotetrakis(4,5-diphenylimidazol-2-yl)porphyrinatonickel(II) **Ni(II)2c** - A mixture of **2a** (0.20 g, 0.13 mmol) and excess nickel(II) acetate (0.10 g) in glacial acetic acid (50 mL) was refluxed during 1h. The acetic acid was removed by vacuum distillation to give a violet-black residue which was subjected to column chromatography on alumina (eluting with 3% methanolic chloroform). The three atropoisomers co-chromatographed as one band, which on crystallisation with ether afforded the Ni(II) complex of **2a** (0.13 g, 61%). This complex (0.13 g, 0.08 mmol), together with palladium black (0.40 g) were strirred together in 4.4% formic acid in methanol, under N_2, and refluxed during 48 h. The solution was cooled, filtered, and evaporated to dryness to give a deep green solid. This solid was dissolved in ethanol (50 mL), excess of the high-potential quinone DDQ (0.50 g) added, and the mixture refluxed during 24 h. The solution was evaporated to dryness, and the resulting solid taken into the minimum volume of chloroform and chromatographed on alumina (eluting with chloroform. The single deep green band was eluted, concentrated, and crystallised with ether to afford a deep green-black amorphous solid (0.046 g, 46%) of the desired porphyrin **2c**, m.p. >300°C. (Found: C, 75.6; H, 4.5; N, 13.1. $C_{80}H_{52}N_{12}Ni.{}^{3}/_{2}H_2O$ requires C, 75.85; H, 4.35; N, 13.27.) FAB-MS (3-NOBA, TFA): m/z = 1239 (M^++1), requires m/z = 1239. λ_{max}($CHCl_3$) ($\varepsilon/10^3$, l $mol^{-1}cm^{-1}$): 459(122), 554 (14.7), 600 (9.8). δ_{ppm}(d_6-DMSO): 13.32 (s, 4H, imidazole-NH), 9.56 (s, 8H, ß-H), 8.32-7.34 (m, 40H, phenyl-H). IR (KBr) cm^{-1}: 3420 (s, broad, imidazole (H-bonded) N-H stretch), 3088-3013 (w, aromatic C-H stretch) 1604, 1500, 1444, 1338 (m, imidazole and porphyrin C=C, C=N in-plane bend), 1144, 1074, 1029 (m, aromatic C-H in-plane bend), 923 (w, porphyrin macrocylic bend), 788, 766, 696 (m, aromatic C-H out-of-plane bend).

Mesotetrakis(4,5-diphenylimidazol-2-yl)porphyrin **2c** - A solution of **2b** (0.084 g, 0.051 mmol) in a solution of 12M HCl diluted (to 9M) with methanol (50 mL) was refluxed during 48 h and then allowed to cool to room temperature. The resulting precipitate was filtered and washed with methanol, taken into the minimum of DCM, and chromatographed on alumina (eluting with a solution of 1% methanol in DCM). The green eluant (single band) was concentrated and crystallised with ether to afford a deep green solid (0.033 g, 55%) of the desired deprotected porphyrin **2c**, m.p. >300°C (Found: C, 78.6; H, 5.1; N, 13.4. $C_{80}H_{54}N_{12}.2{}^{3}/_{8}H_2O$ requires C, 78.35; H, 4.90; N, 13.71.) FAB-MS (3-NOBA, DCM) m/z = 1183 (M^++1), requires m/z = 1183. λ_{max}(DCM) ($\varepsilon/10^3$, l $mol^{-1}cm^{-1}$): 453 (118), 605 (17.8), 678 (11.3). λ_{max}(DCM + TFA): 511 (177), 747 (74.5). δ_{ppm}(d_6-DMSO): 13.90 (s, 4H, imidazole-NH), 9.53 (s, 8H, ß-H), 7.97-7.34 (m, 40H, phenyl-H), -2.58 (s, 2H, porphyrin-NH). IR (KBr) cm^{-1}: 3408 (m, broad, imidazole (H-bonded) N-H stretch), 3038 (w, aromatic C-H stretch) 1604, 1474, 1444, 1400 (m, imidazole and porphyrin C=C, C=N in-plane bend), 1156, 1072, 1016 (m, aromatic C-H in-plane bend), 970 (w, porphyrin macrocylic bend), 790, 766, 696 (s, aromatic C-H out-of-plane bend).

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