

Unexpected but convenient synthesis of soluble *meso-tetrakis*(3,4-benzoquinone)-substituted porphyrins

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ABSTRACT: A new route to 3,4-benzoquinone-substituted porphyrins is reported. In attempted nitration reactions on the copper(II) or nickel(II) complexes of 5,10,15,20-*tetrakis*(3,5-di-*t*-butyl-4-hydroxyphenyl) porphyrin using lithium nitrate in acetic anhydride-acetic acid/chloroform no nitration products could be detected with the main products being the corresponding complexes of 5,10,15,20-*tetrakis*(3,4-dioxo-5-*t*-butylcyclohexa-1,5-dienyl)porphyrin. These *o*-quinone-substituted porphyrins are available in reasonable yield (>50%), their synthesis is simple and they are of good solubility. The electrochemical and spectroelectrochemical properties of representative *o*-quinone-substituted Cu(II) and Ni(II) porphyrin derivatives are also reported.

KEYWORDS: nitration, benzoquinone, porphyrin, lithium nitrate, oxidation.

INTRODUCTION

Porphyrins substituted with benzoquinone groups were first prepared by Milgrom and coworkers [1–3] who recognized their potential due to the presence of functional moieties similar to those involved in photosynthetic processes, namely porphyrin and quinone. Attachment of a quinone unit to porphyrin led largely to the quenching of fluorescence emission from the latter due to intramolecular processes, and this feature is now generally considered as symptomatic of the occurrence of energy transfer or electron migration [4, 5]. Subsequently, the mechanism involved in converting hydroquinone- or phenol-substituted porphyrins to their quinone analogs was studied intensively [6–8] with the aim of understanding the structures of any free radical intermediates existing between the oxidized and reduced states of these molecules. Additionally, oxidation of phenol-substituted compounds to the corresponding hemiquinonoid-substituted molecules [9–11] has permitted development of a family of highly colored N-substituted tetrapyrroles [12–14] suitable for sensing applications [15–17] and supramolecular chemistry [18–20].

The introduction of a benzoquinone group substituted at a porphyrin moiety has usually been accomplished by preparation of the corresponding *o*-dimethoxyphenylsubstituted compound followed by its demethylation

^oSPP full member in good standing

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Scheme 1. Synthesis of 3,4-dioxo-5-t-butylcyclohexa-1,5-dienyl-substituted porphyrins from metal complexes of 1 and 4. (i) LiNO₃ (~9 equiv.)/CHCl₃/Ac₂O/AcOH/60 °C/3 h. Yield (2): ~50%. (ii) LiNO₃ (~2.5 equiv.)/CHCl₃/Ac₂O/AcOH/60 °C/1.5 h/yield (5): 89%

(using boron tribromide) then oxidation [21] and the utility of this method has also been demonstrated by Senge and coworkers [22, 23]. Oxidation of hydroquinone groups has been achieved in a variety of ways but often simply relies on interaction of the deprotonated species with ambient oxygen. This method can be rather inconvenient since it involves first multiple demethylations in a single step then potentially low yielding oxidation reactions to the quinonesubstituted porphyrins. Additionally, in our experience, handling and purification of, for instance, *tetrakis*(3,4dihydroxyphenyl)porphyrin [24] is not so convenient. In this work, we report a direct access to soluble benzoquinone-substituted porphyrins by an unexpected oxidative dealkylation of 5,10,15,20-tetrakis(3,5-di-tbutyl-4-hydroxyphenyl)porphyrin (1) that yields 5,10,-15,20-tetrakis(3,4-dioxo-5-t-butylcyclohexa-1,5-dienyl) porphyrin (2) (see Scheme 1). This transformation was first observed during attempts to β -nitrate the copper(II) or nickel(II) complexes of 1 using the method for nitration described by Richeter et al. [25]. Products due to stepwise oxidative dealkylation could be detected by thin layer chromatography and mass spectrometry, and the final major products of reactions were the respective Cu(II) and Ni(II) complexes of 2 although products with lower order conversions could also be obtained (e.g. 3b which contains a single unreacted phenol group). Notable features of these compounds are their brown/black colors in the solid and solution states and their excellent solubilities in non-polar solvents due to the remaining *t*-butyl substituents. Additionally, a mono-(o-quinone)-substituted compound (5) could also be prepared by treating the singly (3,5-di-t-butyl-4hydroxyphenyl)-substituted porphyrin 4 in the same manner. This method constitutes a useful method for introducing a metal chelating group at the periphery of porphyrins while maintaining good solubilities of the resulting compounds.

RESULTS AND DISCUSSION

Chemical structures of the compounds prepared in this work are shown in Scheme 1. Notably, they are o-quinone-substituted porphyrins analogous with those prepared by other workers [21, 22, 23, 29]. Quinone-substituted porphyrins have usually been prepared by synthesis of the porphyrin containing the appropriate oligo-methoxylated compound followed by its demethylation usually employing boron tribromide reagent. The method we describe represents an addition to the known procedures to the quinone-substituted porphyrins and is advantageous from the point-of-view that it uses mild reagents so that a metal complex (albeit currently only Cu(II) or Ni(II)) can remain intact during the procedure. During this work it did not prove possible to prepare suitable crystals of any of the o-quinone compounds although we could obtain an X-ray crystal structure of the precursor 4b. This is shown together with a calculated (ChemOffice, Chem3D, MM2) structure of the quinone-substituted porphyrin resulting from its oxidation in Fig. 1.

The black quinone-substituted products have appropriate changes of infrared spectrum in particular the appearance of a strong band around 1660 cm⁻¹ due to the new quinone C=O stretching mode and the disappearance of the hydroxyl stretching mode at 3630 cm⁻¹. Their ¹H NMR spectra have resonances due to *t*Bu groups with the required lower integration values and the former singlet due to the aromatic protons at the



Fig. 1. (a) X-ray crystal structure of precursor 4b and (b) calculated structure (ChemOffice, Chem3D, MM2) of the demetalated form of 5

meso-substituents becomes two peaks due to protons adjacent to quinone and *t*Bu groups, respectively, with appropriate integration values and *meta*-coupling constants. In ¹³C NMR spectra the most obvious change is the appearance of two resonances close to 180 ppm due to the two carbonyl carbon atoms of the *o*-quinone groups. Figure 2 shows spectroscopic data for **5**.

The most interesting characteristic of the new compounds is their intensely brown-black colors in the solid state (black) and solution (brown-black). In fact, even the singly-substituted compound 5 exhibits the same dark hue attesting to the strong effect of the o-quinone substituent on the porphyrin chromophore relative to simple phenyl substituents. Electronic absorption spectra of the compounds are shown in Fig. 3. For compounds 2a and 2b, the extinction coefficients at the B-bands are attenuated to about 50% the value of the parent compounds. Apart from this, the most important feature is the increased absorbance across the entire visible range from 350 to nearly 700 nm, which accounts for their dark colors. The Ni(II) complex 2b has an additional intense band at 290 nm whose origin is not currently understood. For 4a, 4b and 5, there are the expected changes in Q-band structure upon metalation of the porphyrin and, upon oxidation to the benzoquinone, a similar increase in extinction across the visible spectrum from 370-700 nm. This latter feature again confers a dark brown color on 5 despite its only bearing one o-quinone functionality.



Fig. 2. Spectroscopic data for oxidized products revealing the characteristics before and after transformation of the 3,5-di-*t*-butyl-4-hydroxyphenyl substituents to *o*-quinone groups. (a) FT-infrared spectra of (i) **4a** (note OH (str.) 3632 cm⁻¹, NH (str.) 3316 cm⁻¹). (ii) **4b** (note OH (str.) 3632 cm⁻¹). (iii) **5** (note absent OH (str.) and C=O (str.) 1660 cm⁻¹). (b) ¹³C NMR spectra of **4b** (lacking C=O) and **5** with two unique carbonyl carbon atoms as required. (c) ¹H NMR spectra of **1b** and **2b** revealing the symmetry breaking of the *meso*-substituent

Electrochemical and spectroelectrochemical data for **2a** and **2b** are shown in Fig. 4. In agreement with our earlier report [30], the potential corresponding to the reductions of *o*-quinone entities appears at -0.30 V vs. Ag/AgCl. In this case, the peak is broadened due to the presence of four quinone entities although reductions



Fig. 3. Electronic absorption spectra of compounds 2–5. Top:
2a (solid line) and 2b (dashed line). Bottom: 4a (dotted line),
4b (dashed line) and 5 (solid line)

are reversible as confirmed by cyclic voltammetry. This suggests occurrence of step-wise electron transfer in a narrow potential window rather than one-step fourelectron transfer. Scanning the potential more in the cathodic direction revealed the second quinone based reductions centred at -1.01 V and -0.89 V vs. Ag/AgCl, respectively, for 2a and 2b (Figs 4a(ii) and 4b(ii)). Scanning the potential in the positive direction revealed the first porphyrin based oxidation at 1.44 V for 2a and 1.30 V for 2b vs. Ag/AgCl respectively. These oxidations were more difficult compared to simple Cu and Ni porphyrins [31] due to the presence of the four electron deficient o-quinone entities directly attached to the porphyrin macrocycle. This point (together with the relative ease of reduction of 2a and 2b) also suggests a reason why nitration of the metalloporphyrin core does not occur in this case, *i.e.* the rapid oxidation during reaction of the phenol substituents to electron withdrawing o-quinone groups suppresses macrocyclic nitration since it is an electrophilic process. We also considered the band gap and estimated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. For 2a and 2b, the estimated values are similar with an optical band gap around 1.8 eV. The electrochemical band gap is probably less reliable since it depends on somewhat broad multiple electron processes and is narrower at ~1.6 eV. LUMO level estimated from onset of the first reduction is at -4.19 eV leading to a



Fig. 4. Electrochemical and spectroelectrochemical data. (a) **2a** (i) differential pulsed voltammogram (ii) electronic absorption spectra under reduction at -0.8 V and (iii) oxidation (+1.7 V). **2b** (i) differential pulsed voltammogram (ii) electronic absorption spectra under reduction at -0.8 V and (iii) oxidation (+1.7 V).

HOMO level (obtained by subtracting the value of the optically estimated band gap) of -5.99 eV. These values suggest that these compounds may be of use either as electron acceptor components of dye-sensitized solar cells (DSSCs) or bulk heterojunction (BHJ) solar cells. For comparison, the C_{70} fullerene derivative PC₇₀BM has LUMO and HOMO levels respectively of -4.3 eV and -6.1 eV [32].

Additional spectroelectrochemical studies confirmed the assigned site of electron transfer. During controlled potential spectroelectrochemistry at -0.5 V (Figs 4a(ii) and 4b(ii)), both compounds appear to obtain electronic absorption spectra similar to their respective metallotetraphenylporphyrins with the expected Q-band structure around 530 nm and a well-defined shift in B-band wavelength from 405 nm to that usual for the respective metal complexes around 420 nm. This is perhaps predictable since the meso-cyclohexadienyl substituents regain their status as phenyl groups. It is likely that the cyclohexadienyl groups are relatively strongly electron withdrawing leading to the hypsochromic shift in the B-band for the quinone-substituted porphyrins. The increased absorbance across the visible spectrum may be due to increased electronic delocalisation (or increased quinonoid character) of these compounds. Under oxidation (+1.6 V, Figs 4a(iii) and 4b(iii)), there are substantial reductions in the B-band intensities for

both compounds and appearance of new bands at 448 nm (2a) and 500 nm (2b); to a large extent these spectral changes were irreversible. The origins of the new spectra under oxidation are not fully understood but could be due to oxidative ring cleavage reactions of the oxidized porphyrin macrocycle, or further oxidative dealkylation involving the remaining *t*-butyl groups or reactions with o-quinone substituents.

There are two unexpected aspects of the reaction and products described here. First, oxidative dealkylation occurs at the phenolic meso-substituents. Second, nitration was not observed to occur to any observable extent either at the porphyrin macrocycle or at mesosubstituents. These features suggest that conversion of 3,5-di-t-butyl-4-hydroxyphenyl groups to 3,4-dioxo-5cyclohexa-1,5-dienyl groups deactivates the porphyrin against this mild nitration process. In fact, even in the case of the mono-3,5-di-t-butyl-4-hydroxyphenyl-substituted compound **4b** nitration of the porphyrin macrocycle was also not observed to occur so that even the presence of a single meso-3,4-benzoquinone appears sufficient to preclude nitration at the porphyrin β -positions. Presumably, the electron-withdrawing effect of even a single benzoquinone group reduces the propensity of the macrocycle to undergo electrophilic substitution. The exclusion of lithium nitrate from the reaction mixture (*i.e.* using acetic acid-acetic anhydride or either of these reagents alone) leads to no reaction and the starting metalloporphyrin only was isolated. Thus, the presence of the nitrating reagent is required for the reaction to the o-quinone to occur. In fact, formation of o-quinones by treatment of sterically hindered phenols with nitrating reagents has been reported [33, 34]. In those cases, initial reaction involving an oxygen atom of a reactive NO₂ species at the *t*-butyl group adjacent to the phenol is followed by elimination of NO and the *t*-butyl group (as isobutene) and leads to formation of o-quinone. This reaction proceeds very rapidly and, if as we suppose a single benzoquinone substituent suppresses nitration at the porphyrin macrocycle, this explains the lack of porphyrin nitration products. Although the lack of any nitrated products suggests that the presence of a single o-quinone substituent is sufficient to suppress nitration at the metalloporphyrin β -positions, we investigated this point by performing the reaction on a nickel(II) porphyrin substituted with a single 3,5-di-t-butyl-4-hydroxyphenyl group. Reaction to the o-quinone-substituted porphyrin occurred rapidly and cleanly with virtually no other products including β -nitro compounds. Even addition of an excess of nitrating agent did not yield the expected β -nitro derivatives. Since we have a general interest in the phenol antioxidant substituted porphyrins it is likely that this method for conversion from 3,5-di-t-butyl-4-hydroxyphenyl to the corresponding o-quinone will provide a useful and selective synthetic route for preparation of unusual peripherally substituted porphyrins.

Introduction of the benzoquinone group as a substituent of porphyrins in turn introduces the possibility of preparing heterometallic complexes [21, 29] where the macrocycle binds, for instance, Ni(II) or Cu(II) leaving the quinone moiety available to bind a different metal cation. In some cases, complexation at quinone can lead to formation of semiquinone type coordination compounds perhaps permitting electronic and magnetic coupling between the nuclei. Formation of semiquinone radical substituents has already been demonstrated for benzoquinone-substituted porphyrins although in that case diamagnetic Zn(II) cations were present at both coordination sites. In the course of this work we found that the Cu(II) and Ni(II) complexes gave by far the best yields of compounds described here. Other first row transition metal complexes, although obviously behaving similarly to the Cu(II) and Ni(II) analogs (judging by the brown/ black colour of the products), so far gave only complex mixtures with no major product. It is currently unclear why only Cu(II) or Ni(II) complexes lead to reasonable yields of the *o*-quinone-substituted products. Finally, we note that transition metal complexes of o-quinone ligands make a major class of transition metal complexes and we are looking forward to using the present system to bridge between the photophysical features of the porphyrins and the exceptional properties of the o-quinone (esp. semiquinone) metal complexes.

EXPERIMENTAL

General

Solvents and reagents were obtained from Aldrich Chemical Co., Fischer Chemical Co., Wako Chemical Co., Tokyo Kasei Chemical Co. or Kanto Chemical Co. ¹H (300.01 MHz) and ¹³C (75 MHz) NMR spectra were measured at 298 K from CDCl₃ or CDCl₃/ d_6 -DMSO solutions of the samples using a JEOL model AL300BX spectrometer with tetramethylsilane as reference. Electronic absorption spectra were measured from dichloromethane solutions of the samples using a Shimadzu model UV-3600 UV/ vis/NIR spectrophotometer. FTIR spectra were measured from samples cast on a barium fluoride disc using a Nicolet model 760X FTIR spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) were measured using a Shimadzu-Kratos model Axima CFR+ mass spectrometer with dithranol as matrix. Cyclic voltammograms were recorded using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas. Spectroelectrochemical measurements were performed either on a Princeton Applied Research (PAR) diode array rapid scanning spectrometer or a Shimadzu UV-visible spectrophotometer using a homemade cell with optically transparent (platinum mesh) electrodes. All the experiments were carried out at 23 ± 1 °C.

Synthesis

1 and its metal complexes were prepared according to previously reported methods [26]. Nitration was attempted by the method of Richeter et al. [25] by addition of 9-12 fold excesses of lithium nitrate dissolved in a ~50:50 v/v mixture of acetic acid and acetic anhydride to ~2 mM solutions of the appropriate porphyrin in chloroform. Reaction progress was monitored using thin layer chromatography (silica plates; CH₂Cl₂/1-2% CH₃OH). Complexes of 2 and 3 were isolated by column chromatography on silica gel eluting with dichloromethane/1-2% methanol or using preparative thin layer chromatography with the same solvent system. 4 was prepared as a by-product from another project [27] and it was prepared as its Ni(II) complex by using the acetate method with monitoring by t.l.c. (silica; CH₂Cl₂). Final purification was achieved by using column chromatography (silica; CH₂Cl₂) yielding 4b which was subjected to nitrating conditions with monitoring using t.l.c. (silica; CH₂Cl₂).

Preparation of 5,10,15,20-*tetrakis*(3,4-dioxo-5-*t*butylcyclohexa-1,5-dienyl)porphyrinatocopper(II) (2a). 5,10,15,20-*tetrakis*(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrininatocopper(II) (0.5 g, 0.42 mmol) was dissolved

in chloroform (200 mL) and was warmed to 60 °C with stirring. A solution of lithium nitrate (0.26 g, 3.77 mmol, ~9 equiv.) in a mixture of acetic acid (50 mL, 0.87 mol) and acetic anhydride (50 mL, 0.525 mol) was added dropwise over a period of 3 h with monitoring of the reaction mixture using thin layer chromatography (silica plates; CH₂Cl₂/1-2% CH₃OH). The reaction mixture was then allowed to cool to ambient temperature then neutralized by careful addition of aqueous saturated NaHCO₃. The mixture was partitioned and the chloroform layer collected then dried (anhydrous Na₂SO₄) and the solvents removed under reduced pressure. The resulting black residue was applied to a silica gel column and chromatographed eluting with CH₂Cl₂/1–2% CH₃OH. The highest yield brown/black band (judging from t.l.c.) was collected (following the elution of products still containing phenol groups). Solvent was removed by evaporation under reduced pressure. A more pure sample for analyses was obtained by preparative thin layer chromatography on silica. 2a: black amorphous powder. Yield 56% (240 mg). UV-vis (CHCl₃): λ , nm $(\epsilon, M^{-1}.cm^{-1})$ 401 (182,400), 501 (35,200), 621 (18,900). FT-IR (BaF₂): v, cm⁻¹ 2959.8, 2920.3, 2869.9 (m, all C-H str.), 1660.2 (s, C=O str), 1562.9 (w), 1536.4 (w), 1482.6 (w), 1466.8 (w), 1367.6 (m, C-H def.), 1342.5 (m, C-H def.), 1297.8 (m), 1267.3 (m), 1238.2 (m), 1207.3 (w), 1144.7 (w), 1081.7 (w), 998.3 (m), 955.3 (m), 909.6 (m), 880.9 (w), 826.4 (w), 798.3 (m). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 1.34 (s, br, *t*Bu-H), 6–8 (br., Ar-H). HRMS (ESI): m/z 1020.2994 (calcd. for C₆₀H₅₁N₄O₈Cu $[M - H]^{-} m/z$ 1020.2985).

Preparation of 5,10,15,20-tetrakis(3,4-dioxo-5-tbutylcyclohexa-1,5-dienyl)porphyrinatonickel(II) (2b). This was obtained in a similar manner to 2a as a byproduct. 2b: black amorphous powder. Yield 44% (188 mg). UV-vis (CHCl₃): λ, nm (ε, M⁻¹.cm⁻¹) 275 (107,000), 397 (145,000), 511 (36,000), 635 (17,000). FT-IR (BaF₂): v, cm⁻¹ 2959.1, 2919.9, 2869.2 (m, all C–H str), 1660.0 (s, C=O str), 1625.0 (m), 1561.9 (w), 1541.8 (w), 1481.8 (w), 1466.8 (w), 1367.7 (m, C-H def.), 1345.6 (m, C-H def.), 1297.6 (m), 1267.7 (m), 1238.2 (m), 1207.5 (w), 1145.6 (w), 1082.3 (w), 1002.8 (m), 956.2 (m), 909.5 (m), 882.9 (w), 826.7 (m), 795.9 (m). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 1.38 (s, 36H, *t*Bu-H), 6.94 (d, ${}^{4}J = 2.10$ Hz, 4H, quinone Ar-H), 7.54 (d, ${}^{4}J = 2.10$ Hz, 4H, quinone Ar-H), 9.28 (s, 8H, β-H). ¹³C NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 29.42 (*t*Bu-methyl), 35.87 (tBu-C), 116.50, 131.95, 132.32, 138.38, 141.05, 149.02, 152.06, 179.31 (C=O), 180.27 (C=O). HRMS (ESI): m/z 1015.3005 (calcd. for C₆₀H₅₁N₄O₈Ni [M - H]⁻ m/z1015.3015).

Preparation of 5-(3,5-di-*t*-butyl-4-hydroxyphenyl)-10,15,20-*tris*(3,4-dioxo-5-*t*-butylcyclohexa-1,5-dienyl)porphyrinatonickel(II) (3b). This compound was obtained as a minor product from the reaction to obtain 2b. 3b: black amorphous solid. Yield < 5%. FT-IR (BaF₂): v, cm⁻¹ 3628.9 (w, O–H str.), 2958.1, 2920.1, 2869.5 (m, all C–H str.), 1660.6 (s, C=O str.), 1635.7 (m, C=C str.),

1562.0 (w), 1541.8 (w), 1481.8 (w), 1466.9 (w), 1433.4 (w), 1367.6 (m, C-H def.), 1346.4 (m, C-H def.), 1299.9 (m), 1267.7 (m), 1237.7 (m), 1147.4 (w), 1121.8 (w), 1080.2 (w), 1003.9 (m), 956.0 (w), 910.3 (w), 883.6 (w), 826.5 (w), 797.2 (m). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 1.36 (s, 18H, tBu-H, quinone adj. to phenol), 1.37 (s, 9H, tBu-H, quinone opp. phenol), 1.56 (s, 18H, tBu-H, phenol), 5.59 (s, 1H, phenol O-H), 6.94 (d, ${}^{4}J = 2.10$ Hz, 3H, quinone Ar-H), 7.56 (d, ${}^{4}J = 2.10$ Hz, 3H), 7.78 (s, 2H, phenol Ar-H, quinone Ar-H), 8.96 (d, ${}^{3}J = 5.10$ Hz, 2H, β -H), 9.11 (d, ${}^{3}J = 4.80$ Hz, 2H, β-H), 9.23 (s, 4H, β-H). ¹³C NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 29.39 (tBu methyl, quinone), 30.55 (tBu methyl, phenol), 34.58 (tBu-C, phenol), 35.76 (tBu-C, quinone), 115.17, 115. 70, 119.82, 123.56, 130.54, 130.78, 131.01, 131.44, 131.63, 131.69, 134.84, 134.88, 135.04, 138.68, 140.21, 140.55, 144.73, 148.52, 152.63, 179.53 (C=O), 180.41 (C=O). MALDI-TOF-MS (dithranol): m/z 1058.38 (calcd. for C₆₄H₆₄N₄O₇Ni [M + 2H]⁺ m/z 1058.41).

Preparation of 5-(3,5-di-t-butyl-4-hydroxyphenyl)-10,15,20-triphenylporphyrin (4a). This compound remained from another project [26]. UV-vis (CHCl₃): λ , nm (ϵ , M⁻¹.cm⁻¹) 420 (400,500), 517 (20,100), 554 (13,100), 590 (9,300), 648 (9,600). FT-IR (BaF₂): v, cm⁻¹ 3631.8 (m, O–H str.), 3316.4 (m, N–H str.), 3054.7, 3024.6 (w, C-H str.), 2957.1, 2908.3 (m, C-H str.), 1596.7 (w, C=C str), 1556.0 (w, C=C str.), 1470.3 (m, C-H def.), 1440.4 (m), 1430.9 (m), 1399.9 (w), 1350.2 (m), 1311.1 (w), 1226.9 (m), 1186.4 (w), 1176.9 (w), 1154.2 (m), 1121.1 (w), 1071.4 (w), 1031.4 (w), 1001.7 (m), 971.9 (m), 963.4 (m), 926.9 (w), 889.5 (w), 874.6 (w), 847.2 (w), 800.4 (s). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ, ppm -2.77 (br. s, 2H, NH), 1.63 (s, 18H, tBu-H), 5.55 (s, 1H, phenol O-H), 7.75 (m, 9H, phenyl-H), 8.04 (s, 2H, phenol Ar-H), 8.23 (m, 6H, phenyl-H), 8.40 (m, 6H, β -H), 8.93 (d, ^{3}J = 4.50 Hz, 2H, β -H). MALDI-TOF-MS (dithranol): m/z 743.35 (calcd. for $C_{52}H_{47}N_4O [M + H]^+$ m/z 743.37).

Preparation of 5-(3,5-di-t-butyl-4-hydroxyphenyl)-10,15,20-triphenylporphyrinatonickel(II) (4b). 4a (0.25 g, 0.34 mmol) was dissolved in chloroform (70 mL) and warmed to 50 °C. A solution of nickel(II) acetate tetrahydrate (0.4 g, 1.61 mmol) in methanol (10 mL) was then added and the mixture was brought to reflux. Heating was continued for 8 h then the solvents were removed under reduced pressure. The resulting red-orange residue was subjected to column chromatography (silica; CH₂Cl₂). Product containing fractions were combined and solvents were removed under reduced pressure and the product recrystallized by dissolving in dichloromethane (20 mL) and layering the resulting solution with the same volume of methanol. Crystals suitable for single crystal X-ray analysis were obtained by a further crystallization on a smaller scale using the same method. 4b: red-purple crystalline plates. Yield 85% (228 mg). UV-vis (CHCl₃): λ, nm (ε, M⁻¹.cm⁻¹) 418 (273,600), 530 (25,000). FT-IR (BaF₂): v, cm⁻¹ 3631.9 (m, O–H str.), 3055.5, 3024.7 (w, C-H str.), 2957.2, 2910.6, 2871.1 (m, C-H str.), 1599 (m, C=C str.), 1574.4 (w), 1546.9 (w), 1440.11 (m), 1433.2 (m), 1391.1 (w), 1352.7 (m), 1311.4 (m), 1223.9 (m), 1205.2 (w), 1177.5 (w), 1155.0 (m), 1121.3 (m), 1073.2 (m), 1006.1 (s), 942.9 (w), 889.1 (w), 832.9 (w), 825.8 (w), 797.7 (s), 751.8 (m). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 1.57 (s, 18H, *t*Bu-H), 5.48 (s, 1H, phenol O-H), 7.66 (m, 9H, phenyl-H), 7.82 (s, 2H, phenol Ar-H), 8.01 (m, 6H, phenyl-H), 8.73 (s, 4H, β -H), 8.74 (d, ^{3}J = 4.80 Hz, 2H, β -H), 8.83 (d, ${}^{3}J$ = 5.10 Hz, β -H). ${}^{13}C$ NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 30.62 (*t*Bu methyl), 34.55 (tBu-C), 118.66, 118.80, 120.55, 126.86, 127.69, 131.09, 131.95, 132.03, 132.08, 132.62, 133.72, 134.22, 134.31, 134.55, 141.06, 142.53, 142.65, 143.26, 153.61. MALDI-TOF-MS (dithranol): m/z 797.60 (calcd. for $C_{52}H_{45}N_4ONi [M-H]^+ m/z 797.28).$

Preparation of 5-(3,4-dioxo-5-t-butylcyclohexa-1,5dienyl)-10,15,20-triphenylporphyrinatonickel(II) (5). 4b (168 mg, 0.21 mmol) was treated with lithium nitrate (36 mg, 0.52 mmol, ~2.5 equiv.) using the same method as that leading to **2b** and using proportional volumes of acetic anhydride/acetic acid. The reaction was monitored using t.l.c. (silica; CH_2Cl_2). Upon completion the reaction was neutralized and 5 was isolated by using the same method as for 2b. 5: dark purple microcrystalline powder. Yield 144 mg (89%). UV-vis (CHCl₃): λ , nm $(\epsilon, M^{-1}.cm^{-1})$ 410 (255,000), 528 (19,300), 630 (10,300). FT-IR (BaF₂): v, cm⁻¹ 3102.4, 3055.8, 3025.6, 2994.7 (all weak, C-H str.), 2958.9 (m, C-H str.), 2868.2 (w, C=H str.), 1659.8 (s, C=O str.), 1621.4, 1599.1 (w, C=C str.), 1562.1 (w), 1550.4 (w), 1481.8 (w), 1459.6 (w), 1440.8 (m), 1367.0 (m), 1347.5 (m), 1299.6 (w), 1266.9 (w), 1238.3 (m), 1206.4 (w), 1177.1 (w), 1074.6 (m), 1006.1 (s), 957.2 (w), 908.7 (m), 833.9 (w), 827.7 (w), 797.7 (m), 752.5 (w), 730.8 (w), 698.3 (w). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 1.34 (s, 9H, *t*Bu-H), 6.96 (d, ${}^{4}J = 1.20$ Hz, 1H, quinone H), 7.68 (m, 10H, phenyl-H, quinone H), 7.97 (m, 6H, phenyl-H), 8.72 (s, 4H, β -H), 8.86 (d, ${}^{3}J$ = 5.10 Hz, 2H, β -H), 9.11 (d, ${}^{3}J$ = 4.80 Hz, 2H, β-H). ¹³C NMR (CDCl₃, 300 MHz, 298 K): δ, ppm 29.42 (tBu methyl), 35.65 (tBu-C), 113.89, 119.99, 120.45, 126.84, 126.94, 127.00, 127.97, 128.02, 129.85, 131.27, 132.65, 132.85, 133.46, 133.63, 133.65, 139.29, 139.74, 140.48, 140.50, 143.08, 143.21, 143.41, 147.75, 153.52, 179.97 (C=O), 180.69 (C=O). MALDI-TOF-MS (dithranol): m/z 757.42 (calcd. for C₄₈H₃₄N₄O2Ni [M+H]⁺ m/z 756.20).

X-ray crystallography

Crystals of **4b** suitable for X-ray diffraction were grown by diffusion of hexane into a solution of **4b** in dichloromethane. X-ray data for **4b** were collected at 200 K on a Rigaku XtaLAB P200 diffractometer using graphite-monochromated MoKa radiation. Structure solutions by direct methods and full-matrix least-squares refinement against F^2 (all data) were carried out using the SHELXTL package [28]. The structure was refined as a two component inversion twin. All ordered non-H atoms were refined anisotropically. X-ray crystallography data for **4b**: C₅₂H₄₄N₄NiO, M = 799.63 g.mol⁻¹, space group P-1, a = 6.190(5), b = 10.831(5), c = 32.528(5) Å, α = 80.588(5), β = 85.784(5), γ = 77.922(5)°, U = 2102(2) Å³, Z = 2, ρ_{calcd} = 1.264 mg.m⁻³, μ (MoK $_{\alpha}$) = 0.070 mm⁻¹, 64713 reflections measured, 9816 were unique (Rint. 0.0357); refinement against F2 to wR2: 0.1627, R1 = 0.0650 (8093 reflections with I > 2 σ (I)), 531 parameters.

CONCLUSION

In conclusion, we have observed the unexpected oxidative dealkylation of some metal complexes of 5,10,15,20-*tetrakis*(3,5-di-*t*-butyl-4-hydroxyphenyl)-porphyrin (1), which results directly in the analogous complexes of 5,10,15,20-*tetrakis*(3,4-dioxo-5-*t*-butylcy-clohexa-1,5-dienyl)porphyrin (2) in reasonable yields. These compounds have several significant features including strong electronic absorption across the visible range (they appear almost black in solution and the solid state) and high solubilities leading to easy handling for film formation or other processing, and reversible electrochemical reduction processes.

We are also currently investigating the synthesis of discrete heterometallic complexes of these porphyrins in order to investigate magnetic interactions between macrocyclic core metal cation and those complexed at the rather remote periphery of these molecules. We believe that the inter-metal-cation coupling interactions will be mediated by semiquinone radicals where an appropriate metal cation is complexed at the benzoquinone moieties. Details of the structures as well as the catalytic and magnetic properties of these complexes will be reported later. We note that *o*-quinones are a versatile starting point for other functionalities including ring-fused or ring-opened products [22, 23]. We will also report our investigations of those possibilities in due course. Finally, several other 3,5-di-t-butyl-4-hydroxyphenyl-substituted chromophores are available in our laboratory including phthalocyanine, corroles and porphyrins with the antioxidant groups not directly attached to the macrocycle. We will shortly report on the transformations of those compounds in the context of the reaction reported here.

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Supporting information

¹H and ¹³C NMR spectra for new compounds; atomic coordinates for calculated structure of the free base form of **5**; crystallographic information file for **4b** (Figs S1–S9) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-956468. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_ request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

REFERENCES

- Dalton J and Milgrom LR. J. Chem. Soc., Chem. Commun. 1979; 609–610.
- Chan AC, Dalton J and Milgrom LR. J. Chem. Soc., Perkin Trans. 2 1982; 707–710.
- Milgrom LR. J. Chem. Soc., Perkin Trans. 1 1984; 1483–1487.
- 4. Kurreck H and Huber M. Angew. Chem. Int. Ed. Eng. 1995; **34**: 849–866.
- Kang YK, Iovine PM and Therien MJ. Coord. Chem. Rev. 2011; 255: 804–824.
- Traylor TG, Nolan KB and Hildreth R. J. Am. Chem. Soc. 1983; 105: 6149–6151.
- Golder AJ, Milgrom LR, Nolan KB and Povey DC. J. Chem. Soc., Chem. Commun. 1987; 1788–1790.
- Milgrom LR, Yahioglu G and Jogiya NN. Free Radical Res. 1996; 24: 19–29.
- 9. Milgrom LR. Tetrahedron 1983; 39: 3895–3898.
- Golder AJ, Milgrom LR, Nolan KB and Povey DC. J. Chem. Soc., Chem. Commun. 1989; 1751–1753.
- Milgrom LR, Hill JP and Dempsey P. *Tetrahedron* 1994; **50**: 13477–13484.
- Milgrom LR, Hill JP and Yahioglu G. J. Heterocycl. Chem. 1995; 32: 97–101.
- Hill JP, Hewitt IJ, Anson CE, Powell AK, McCarthy AL, Karr P, Zandler M and DSouza F. J. Org. Chem. 2004; 69: 5861–5869.
- 14. Hill JP, Schmitt W, McCarty AL, Ariga K and DSouza F. *Eur. J. Org. Chem.* 2005; 2893–2902.
- Hill JP, Schumacher AL, DSouza F, Labuta J, Redshaw C, Elsegood MRJ, Aoyagi M, Nakanishi T and Ariga K. *Inorg. Chem.* 2006; 45: 8288–8296.

- Shundo A, Labuta J, Hill JP, Ishihara S and Ariga K. J. Am. Chem. Soc. 2009; 131: 9494–9495.
- Labuta J, Ishihara S, Šikorský T, Futera Z, Shundo A, Hanyková L, Burda JV, Ariga K and Hill JP. *Nat. Commun.* 2013; DOI: 10.1038/ncomms3188
- Xie Y, Hill JP, Schumacher AL, Sandanayaka ASD, Araki Y, Karr PA, Labuta J, DSouza F, Ito O, Anson CE, Powell AK and Ariga K. *J. Phys. Chem. C* 2008; **112**: 10559–10572.
- Geng F, Gao H, Meng Q, Dong Z, Wakayama Y, Akada M, Ariga K and Hill JP. *Chem. Commun.* 2011; 47: 8533–8535.
- Subbaiyan NK, Hill JP, Ariga K, Fukuzumi S and D'Souza F. Chem. Commun. 2011; 47: 6003–6005.
- Jose DA, Shukla AD, Kumar K, Ganguly B, Das A, Ramakrishna G, Palit DK and Ghosh HN. *Inorg. Chem.* 2005; 44: 2414–2425.
- 22. Speck M, Kurreck H and Senge MO. *Eur. J. Org. Chem.* 2000; 2303–2314.
- 23. Senge MO, Hatscher S, Ökten Z and Speck M. *Tetrahedron Lett.* 2003; **44**: 4463–4466.
- 24. Bonar-Law RP. J. Org. Chem. 1996; 61: 3623-3634.
- 25. Richeter S, Jeandon C, Gisselbrecht J-P, Graff R, Ruppert R and Callot HJ. *Inorg. Chem.* 2004; **43**: 251–263.
- 26. Milgrom LR, Jones CC and Harriman A. J. Chem. Soc., Perkin Trans. 2 1988; 71–79.
- 27. Ishihara S, Hill JP, Shundo A, Ohkubo K, Fukuzumi S, Elsegood MRJ, Teat SJ and Ariga K. *J. Am. Chem. Soc.* 2011; **133**: 16119–16126.
- Sheldrick GM. SHELXTL 6.14, Bruker AXS, Inc., 6300 Enterprise Lane, Madison, WI 53719–1173, USA, 2003.
- Schulz D, Mussari CP, Ramanathan KK and Kampf JW. *Inorg. Chem.* 2006; 45: 5752–5759.
- 30. Deviprasad GR, Keshavan B and D'Souza F. J. Chem. Soc., Perkin Trans. 1 1998; 3133–3135.
- 31. Kadish KM. Prog. Inorg. Chem. 1986; 34: 435-605.
- Takacs CJ, Sun Y, Welch GC, Perez LA, Liu X, Wen W, Bazan GC and Heeger AJ. J. Am. Chem. Soc. 2012; 134: 16597–16606.
- 33. Astolfi P, Panagiotaki M and Greci L. *Eur. J. Org. Chem.* 2005; 3052–3059.
- 34. Peters SJ, Blood TM and Kassabaum ME. *Eur. J. Org. Chem.* 2009; 6104–6108.