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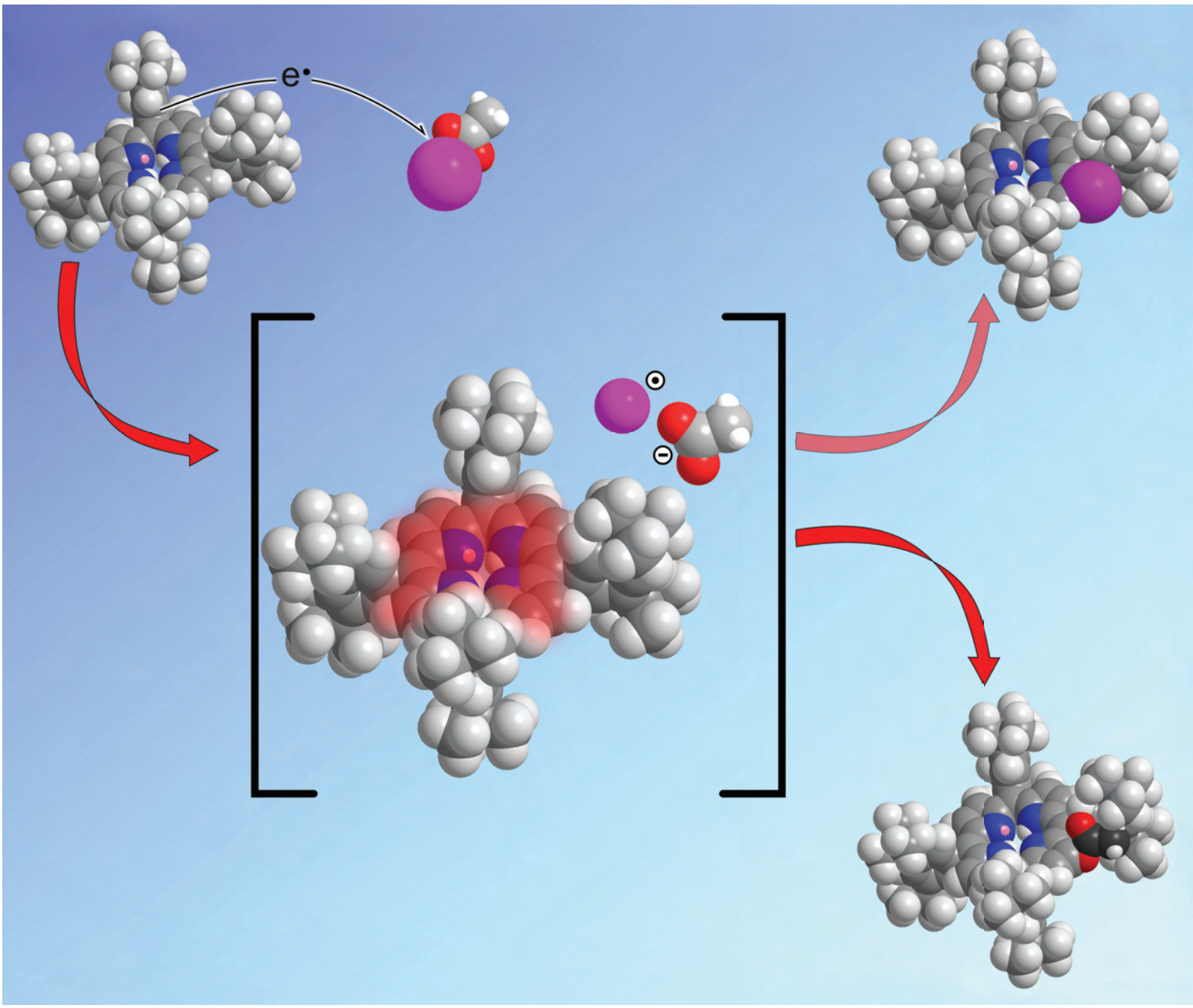

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ARTICLE
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Regiospecific β-functionalization of free-base porphyrins by pseudohalogens

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Pseudohalogens based on iodine ('I–X') can be used to regiospecifically introduce chlorine atoms or acetoxy groups onto the β-positions of *meso*-tetraphenylporphyrins (TPPs). TPPs and a quinoxaline derivative were reacted with iodine monochloride to give mono- or di-chlorinated porphyrins, such that when two chlorine atoms were added they were placed antipodally on the porphyrin ring. Reaction of the porphyrins with a mixture of iodine and silver acetate gave the corresponding mono- and di-acetoxylated porphyrins. The acetoxylated porphyrins could be simply transformed to the corresponding hydroxyporphyrins with subsequent oxidation with the Dess–Martin periodinane, giving a simple new route to chlorin-α-diones and bacteriochlorin-tetraones. From the products of the reactions and a UV–visible spectroscopic study, it is proposed that the reactions proceed *via* a single electron transfer mechanism through a porphyrin cation radical intermediate.

Introduction

The ability to functionalise the porphyrin outer periphery at specific positions under mild conditions is a continuing challenge. Porphyrins have been reported to undergo nucleophilic and electrophilic substitution, as well as radical reactions.[1–4] To get the required control over the porphyrin reactivity it is often necessary to use a metal chelated porphyrin.[1,4] The disadvantage of this is that the final product may be required to have no metal or a different metal chelated. The conditions required to remove the chelated metal have to be compatible with the functionality on the porphyrin outer periphery and this can limit the range of groups that can be introduced. Therefore, methods that can be used to attach functional groups onto the outer periphery of a free-base porphyrin have an advantage as the required metal can be chelated at a later stage of the synthesis. While many of the products isolated from the reactions used to introduce functionality onto the porphyrin outer periphery fit the standard mechanistic rationale, there are the occasional reports where an unusual substitution process occurs. For example, treatment of a 5,15-diphenyl substituted free-base porphyrin with *N*-iodosuccinimide leads to the 'expected' *meso*-iodinated product, arguably by electrophilic substitution, but reaction with iodine monochloride leads to the *meso*-chloro substituted product.[5] This latter product clearly cannot occur *via* a simple substitution reaction. We were therefore interested to understand how this product was formed and to determine if the reaction was specific for *meso* positions, and whether similar reactions could be used for the introduction of other functional groups.

Results and discussion

The first part of our investigation was to determine whether the chlorination was specific for the *meso* positions and for this we chose 5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **1** as the substrate.[1] **1** was chosen as the substrate as the 3,5-di-*t*-butylphenyl groups provide good solubility and protect the *meso* positions from reaction, and the quinoxalino group can direct reaction at the 12- and/or 13-β-pyrrolic positions thus making analysis of the products from the reaction simpler. When **1** was reacted with 2.4 equivalents of iodine monochloride in chloroform heated at reflux (Scheme 1) for four hours, 12-chloro-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **2** was isolated in an excellent yield of 75%. These results show that when the *meso* positions are blocked chlorination can take place on the β-pyrrolic positions. To investigate the generality of the reaction we treated 5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)porphyrin **4** with five equivalents of iodine monochloride in chloroform heated at reflux and this gave 2,12/13-dichloro-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)porphyrin **5** in 58% yield with 11% of the starting material recovered. That is, the method can be used to introduce more than one chlorine atom onto the porphyrin periphery. Importantly both chlorine atoms are attached to the β-pyrrolic positions and the addition of the first chloro group directs the addition of the second antipodally. To determine whether the reaction was specific to the bulky *meso*-3,5-di-*t*-butylphenyl substituted porphyrins we also carried out the dichlorination reaction with the simple, less sterically hindered 5,10,15,20-tetraphenylporphyrin **6**. The reaction was carried out under similar conditions to those used for the formation of **5** and the corresponding 2,12/13-dichloro-5,10,15,20-tetraphenylporphyrin **7** was isolated in a 46% yield with, in this case, a 23% yield of the starting porphyrin recovered. Therefore this methodology can be used to simply and mildly introduce chloro groups onto the periphery of *meso*-tetraphenylporphyrins, opening the avenue for the introduction of new functionalities by nucleophilic substitution reactions.[1] While the mechanism of the chlorination reaction will be discussed in more detail later, it is important to note that chlorination of relatively easily oxidised aromatics has been reported to occur *via* a radical cation intermediate to which either a chloride anion or iodine radical can add and it is likely a similar mechanism is at play here.[6,7] In these simple aromatic systems it has been shown that solvent and steric hindrance can play important roles in the product outcome of the reaction.[6] In the work here, utilising the

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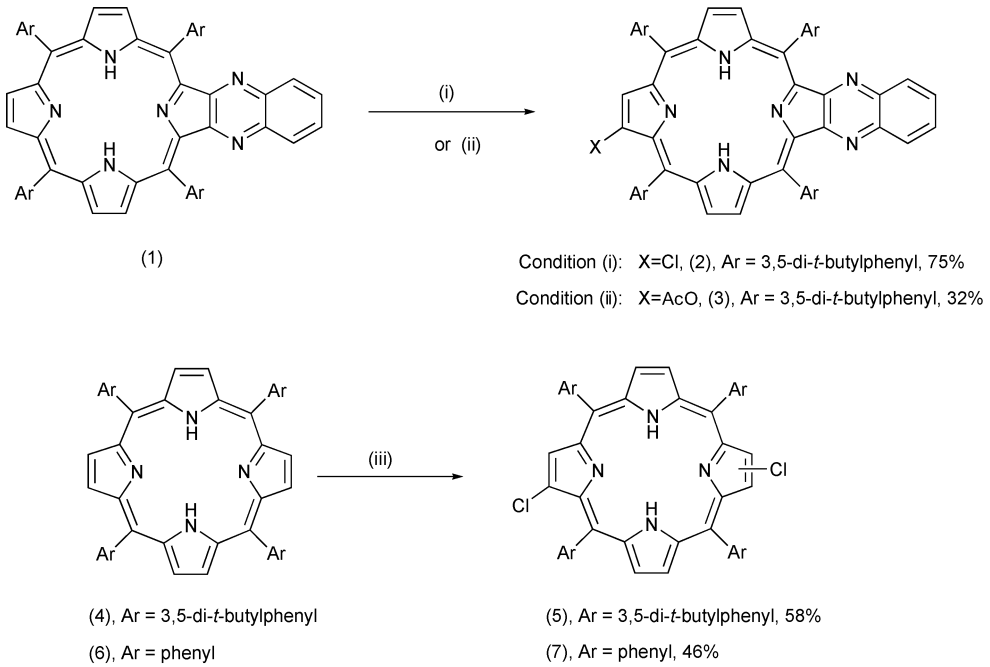


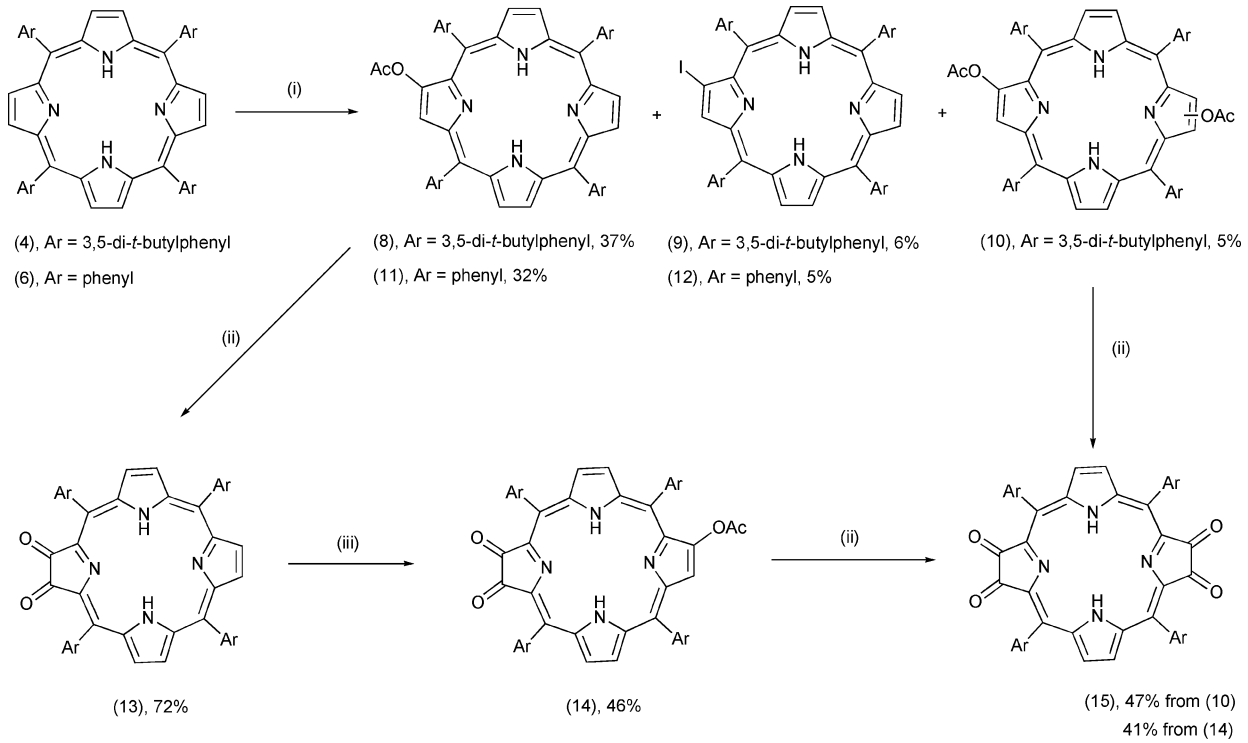
Scheme 1 (i) ICl, $CHCl_3$, reflux; (ii) I_2, AgOAc, $CHCl_3$; (iii) ICl, $CHCl_3$–CH_2Cl_2, reflux.

relatively non-polar chloroform and having the *meso* substituents (phenyl and 3,5-di-*t*-butylphenyl) ensures that the less sterically demanding and more polar chloride anion adds preferentially over the iodine atom. The fact that only the 12-chloro regioisomer is isolated from the reaction of **1** is similar to that observed in other electrophilic or radical reactions of chlorins. In the past this has been simply attributed to the fact that the 18-π electron aromatic pathway imparts alkenyl-like character to the double bond antipodally to the chlorin moiety.[1,8] However, this is not in accord with molecular orbital calculations, which show that the highest occupied molecular orbital density is not preferentially located on the 12- and 13-positions.[9,10] It may be that once the porphyrin is oxidised, the stability of the radical cation is greatest when the 18-π electron aromatic pathway is present, that is, the reaction is under kinetic control. A similar argument could explain the selectivity of the antipodal nature of the addition of the two chloro groups on **4** and **6**.

The *in situ* formation of a porphyrin radical cation intermediate and subsequent nucleophilic attack is not dissimilar to early work on porphyrin substitution reactions where a radical cation was formed *ex situ* and then reacted with a range of nucleophiles.[11] In these earlier studies a zinc chelated *meso*-tetraphenylporphyrin was oxidised and then reacted with a range of anions including nitrite, thiocyanate, pyridine and triphenylphosphine to form the corresponding 2-substituted porphyrins. Interestingly the reaction with the oxygen nucleophiles, methanol and water, caused substitution on the *meso* position in spite of it being sterically encumbered. In a similar vein it was later reported that a nitro group could be introduced onto the β-pyrrolic position of a copper chelated porphyrin by reaction with a mixture of iodine and silver nitrite.[12] Although the mechanism of this latter reaction was not discussed in any detail it was assumed that the reaction occurred *via* an *in situ* oxidation by iodine and subsequent 'substitution reaction' with the nitrite anion. However, it is interesting to note that the iodine–silver nitrite mixture is known to give iodine nitrite.[13] It is therefore possible that the nitration using the iodine–silver nitrite mixture also occurs *via* a similar mechanism to the iodine monochloride reaction. That is, there is a single electron transfer from the porphyrin to iodine nitrite to form a charge transfer complex comprised of the porphyrin radical cation, the iodine atom, and the nitrite ion followed by, under the relatively non-polar solvent conditions, nucleophilic attack of the nitrite ion.

Given that iodine monochloride and iodine–silver nitrite are effectively pseudohalogen 'I–X' reagents we were interested to see whether the methodology could be used to introduce an acetoxy group as the reaction of iodine with silver acetate gives iodine acetate.[14] Simple deprotection could give hydroxyporphyrins, with subsequent oxidation leading to chlorin-α-diones that have been used to build porphyrin arrays.[15–18] We first reacted **1** (Scheme 1) with a mixture of 2.5 equivalents of iodine and 3.8 equivalents of silver acetate in chloroform at room temperature for 1.5 hours. Acetoxylation occurred in the 12-position to give **3** in a 32% yield with 44% of **1** being recovered. In addition, 5% of 12-iodo-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)quinoxalino-[2,3-*b*]porphyrin was also isolated. The fact that both the acetoxy and iodo products were isolated lends strength to the argument that the mechanism involving a porphyrin radical cation is at play. Unlike the iodine monochloride reaction, in this case the acetoxy group and iodine atom are both large and hence there is a reduction in the steric discrimination, with some of the iodo product being formed.

We then extended the methodology to the reaction of the simple free-base porphyrin 5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)-porphyrin **4** with the iodine–silver acetate (1.9 and 2.9 equivalents respectively) mixture (Scheme 2). After 90 minutes at room temperature 2-acetoxy-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)porphyrin **8** was obtained in a yield of 37%. Again the starting porphyrin **4** (36%) was recovered and there was



Scheme 2 (i) I_2, AgOAc, chloroform; (ii) a. K_2CO_3, CH_2Cl_2–MeOH; b. DMP, CH_2Cl_2; (iii) I_2, AgOAc, $CHCl_3$–CH_3COOH.

a small amount (6%) of 2-iodo-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)porphyrin **9**. In addition, 5% of 2,12/13-bisacetoxy-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)porphyrin **10** was also formed. It is interesting to note that, unlike the case of the dichlorination, the second acetoxy group is not exclusively attached antipodally to the first. Nevertheless it was fairly straightforward to separate **10** from **4**, **8** and **9**, as well as the other bis-acetoxylated materials. In an effort to increase the yield of **8** we added a second aliquot of the iodine–silver acetate mixture (to give a total of 4.2 and 6.4 equivalents of each reagent respectively) and this improved the yield of **8** to 47%, with starting material **4** (17%), iodo **9** (7%), and diacetoxy **10** (11%) also being isolated. We found that adding a third aliquot of reagents did result in all the starting material being consumed but this was at the cost of the reduction in yield of the desired **8** to 14% without the concomitant increase in the amount of **10**, which was isolated in a 13% yield. It is noteworthy that, while the acetoxylation occurs predominantly on the β-pyrrolic positions, it is likely that the decomposition pathway involves acetyloxylation of the *meso* carbons.[11] As in the case of the reaction with iodine monochloride, we were interested to see whether the difference in steric bulk between the phenyl and 3,5-di-*t*-butylphenyl *meso* substituents made a significant difference to the product distribution. We reacted the simple *meso*-tetraphenylporphyrin **6** with a similar ratio of iodine and silver acetate (2.5 equivalents and 3.8 equivalents respectively), as in the first reaction of **4**, and the corresponding iodo **12**, starting material **6**, and acetoxyporphyrin **11** were isolated in 5%, 43%, and 32% respectively. This result again shows that the reaction is more general for *meso*-phenyl substituted porphyrin derivatives.

With our interest of using porphyrin-α-diones as building blocks for porphyrin arrays we investigated the conversion of the mono- and di-acetates, **8** and **10** respectively to the chlorin-α-dione **13** and bacteriochlorin-tetraone **15**. Porphyrin acetate **8** was deprotected with methanolic potassium carbonate to give 2-hydroxy-5,10,15,20-tetrakis(3′,5′-di-*t*-butylphenyl)porphyrin, which was then oxidized to the chlorin-α-dione **13** (Scheme 2) using the Dess–Martin periodinane (DMP),[19] giving a 72% yield for the two steps. Using the optimised conditions for the formation of **8** (a yield of 47%), this process gives an overall yield of the chlorin-α-dione **13** of 34% (41% conversion) in three simple steps from **4** rather than the five or six step processes that are normally used. In a similar process the diacetate **10** could be deprotected and oxidised with DMP to give the bacteriochlorin-tetraone in 47% yield, giving an overall three-step conversion of **4** to **15** of 6%. This again is a much more straightforward process than has been reported in the past for the synthesis of **15** and occurs with comparable yields.[20,21] Interestingly the same overall yield of **15** from **4** can be achieved by reacting chlorin-α-dione **13** with the iodine–silver acetate mixture with subsequent deprotection and DMP oxidation. Chlorin-α-dione **13** was converted to the corresponding acetoxychlorin-α-dione **14** in 46% yield using acidified chloroform with the subsequent deprotection and oxidation to bacteriochlorin-tetraone **15** (Scheme 2) occurring in 41% yield. The bacteriochlorin-tetraone **15** was therefore synthesised in a 6% yield for the six steps from **4**.

While the chlorination and acetoxylation reactions of the porphyrin outer periphery seem to be reasonably general, it is interesting to consider in more detail how the reactions proceed. Electrophilic substitution can be discounted, as it would be the iodine that would add in each case, as chlorine and oxygen are more electronegative than iodine. Clearly it cannot be simple nucleophilic substitution as there is there no leaving group on the porphyrin ring and no activating chelating metal. As has been stated earlier the chlorination, as opposed to iodination, of relatively easily oxidised aromatic rings by iodine monochloride

can occur *via* a single electron transfer pathway.[6,7] That is, in the first step the iodine monochloride forms a π- or encounter complex with the aromatic ring, and then an electron is transferred from the aromatic ring (oxidation) to the iodine monochloride to give an intermediate charge transfer complex comprised of the radical cation of the aromatic ring, the chloride anion, and the iodine atom. This intermediate complex can then collapse by one of two pathways. The first pathway involves the iodine atom adding to the radical cation to form the iodo-substituted aromatic cation. Subsequent loss of the proton forms the neutral iodo-substituted aromatic ring with hydrogen chloride as the by-product. In the second pathway the chloride anion adds giving the chloro-substituted aromatic radical, which is oxidised by a second equivalent of iodine monochloride to the corresponding cation. Loss of a proton leads to the chloro-substituted ring and iodine and hydrogen chloride are the initial by-products. We have illustrated the equivalent pathway for a porphyrin substrate in Fig. 1 and, based on the observed product outcomes, believe that this is the most likely mechanism for the formation of the chlorinated porphyrins.

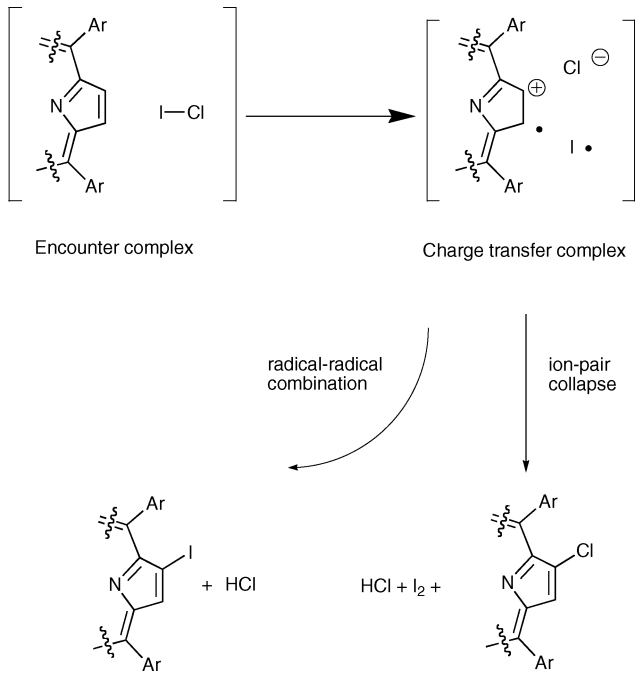


Fig. 1 Possible mechanism for the formation of the chlorinated product from the reaction of the porphyrins with ICl.

In an effort to gather further evidence that this is the mechanistic pathway, we first attempted to follow the chlorination of **4** spectroscopically with the reaction carried out *in situ* in chloroform under the normal conditions, to see whether the absorption spectrum of the radical cation could be observed. However, in common with other reactive aromatic substrates, the reaction at room temperature was too fast to allow observation of the absorption spectrum of the intermediate radical cation and all that was seen was the absorption spectrum of a protonated porphyrin. Analysis of the solution by thin layer chromatography (TLC) showed that a chlorinated product had formed. In one study on the reaction of iodine monochloride with aromatic substrates it was reported that 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) could be used to stabilise the radical intermediate in an iodine monochloride reaction.[22] We therefore carried out the reaction of porphyrin **4** with iodine monochloride in HFP. The absorption spectra at the different stages are shown in Fig. 2. However, interpretation of the results was not straightforward as the porphyrin and HFP have similar pK_as of around 9.3.[23] This meant that when porphyrin **4** was dissolved in HFP it was protonated and the solution turned green [(i) in Fig. 2]. On addition of the iodine monochloride the colour of the solution changed to red and two new peaks were observed in the absorption spectrum at 549 nm and 715 nm [(ii) in Fig. 2]. The spectrum did not change appreciably over a period of a couple of hours, but on heating the peak at 549 nm disappeared while the longer wavelength peak remained [(iii) in Fig. 2] and the solution turned green. The peak at 715 nm is close to that observed for porphyrin **4** dissolved in HFP and treated with hydrogen chloride (679 nm) and so is probably associated with a protonated product. TLC analysis of the heated solution showed that a chlorinated product was present. That is, the peak at 715 nm in (ii) of Fig. 2 may just arise from product formation on the initial addition of the iodine monochloride. The fact that the peak at 549 nm disappears during product formation may imply that it is the signature of an intermediate, which we propose could be the porphyrin radical cation.

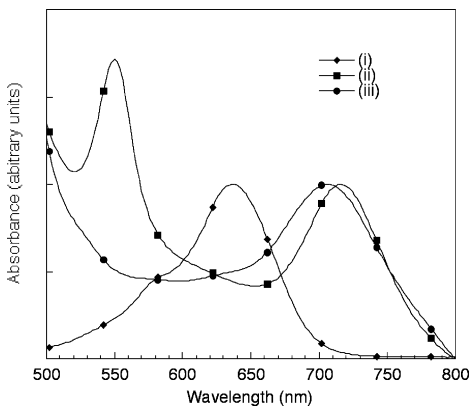


Fig. 2 UV–visible spectra of **4**: (i) in HFP, (ii) 2.5 h after addition of ICl, and (iii) after heating. The spectra have been normalised for clarity.

If the chlorination and acetoxylation go *via* a similar mechanism then we might expect to see a similar absorption for the intermediate in the latter reaction. We therefore carried out a spectroscopic study of **4** with the iodine–silver acetate mixture, and the absorption spectra for the sequence of steps is shown in Fig. 3. This work was complicated by the fact that iodine is not soluble in HFP. Indeed, addition of iodine to HFP caused no change in the absorption spectrum of the protonated porphyrin (not shown). However, on addition of silver acetate the spectrum of the solution changed and there was a peak at 530 nm [(ii) in Fig. 3], which is very close to the new peak observed during the iodination reaction. In this case there was no absorption at longer wavelength and even heating the reaction resulted in no acetoxylated product being observed, even though a new absorption due to protonated porphyrin **4** was seen [(iii) in Fig. 3]. The fact that no reaction was observed is perhaps not surprising as it known that HFP reduces the reactivity of nucleophiles (it is how the radical cation is 'stabilised') and the acetate is a relatively poor nucleophile. Therefore, since the reactions of **4** with iodine monochloride and iodine and silver acetate lead to the chlorinated and acetoxylated materials as the main products, and the intermediates that are

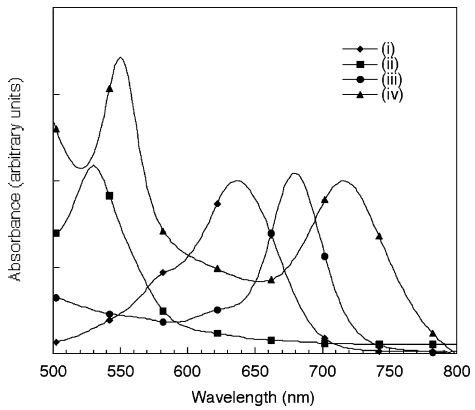


Fig. 3 UV–visible spectra of **4**: (i) in HFP, (ii) 1.5 h after addition of I_2–AgOAc, (iii) after heating, and (iv) 2.5 h after addition of ICl for comparison. The spectra have been normalised for clarity.

formed on the addition of the reagents have absorptions in the UV–visible spectra at similar wavelengths, this strongly suggests that these reactions proceed *via* a single electron transfer mechanism through a porphyrin radical cation intermediate.

Experimental

^{1}H NMR spectra of new compounds were recorded on Brüker DPX-400 (400 MHz), Brüker DQX-400 (400 MHz), or Brüker AMX-500 (500 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent peak. Multiplicities are reported as broad (br), singlet (s), doublet (d), doublet of doublets (dd), or multiplet (m) and coupling constants are reported to the nearest half Hz. Infrared spectra were recorded using a KBr disc using a Perkin-Elmer Paragon 1000 IR spectrometer or a Brüker Tensor 27 FT-IR spectrometer. Values of the absorption maxima are recorded in wavenumbers (cm^{-1}). UV–vis spectra were measured in spectrophotometric grade dichloromethane with a Perkin-Elmer Lambda 14P UV–vis spectrometer. The absorption peaks are reported with 'sh' indicating a shoulder. Mass spectra were recorded on a Micromass Platform for ESI, or a Walters LCT Premier ESI-ToF mass spectrometer. Accurate masses were measured on a Brüker MicroToF or a Micromass LCT spectrometer. Values for m/z are quoted in Daltons. Melting points were measured using a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were performed by Mr Stephen Boyer in SACS, London Metropolitan University.

Petroleum spirit with a boiling point range of 40 to 60 °C is referred to as light petroleum. Chloroform required for the halogenation reactions was filtered through a short column of neutral alumina (Brockmann activity 1; 150 mesh) purchased from Aldrich. Chloroform required for the acetoxylation reactions was filtered through a short column of acidic alumina (Brockmann activity 1; 0.05–0.15 mm) purchased from Fluka. All other reagents were purchased from commercial sources and used without further purification. Where solvent mixtures are used, the proportions are given in terms of volume. Thin layer chromatography was performed with Merck aluminium plates coated with silica gel F_{254}. Column chromatography was performed using the flash chromatography technique, with ACROS Organics silica gel 0.035–0.07 mm.

12-Chloro-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin 2

A solution of iodine monochloride in chloroform (0.02 M, 2.5 cm^3, 0.050 mmol) was added to a refluxing solution of 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin **1** (45 mg, 0.039 mmol) in chloroform (10 cm^3). After 2 h a further aliquot of iodine monochloride in chloroform (0.02 M, 2.5 cm^3, 0.050 mmol) was added. The reaction mixture was heated at reflux for a further 2 h and then allowed to cool to room temperature. Saturated aqueous sodium thiosulfate solution (100 cm^3) was added and the organic layer was separated. The organic layer was washed with saturated sodium thiosulfate solution (100 cm^3), dried over sodium sulfate, filtered and the solvent was removed. The crude product was purified by column chromatography over silica using a dichloromethane :light petroleum (1 : 8) mixture as eluent to give **2** (35 mg, 75%) as a dark purple solid, mp >280 °C; found: C, 82.1%; H, 8.0%; N, 6.9%; $C_{82}H_{95}ClN_6$ requires C, 82.1%; H, 8.0%; N, 7.0%; λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 299 (4.44), 337sh (4.54), 357 (4.61), 409sh (5.17), 435 (5.47), 530 (4.45), 568sh (3.75), 599 (4.16), 653 (3.00); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.72 and −2.59 (2 × 1H, br s, NH), 1.480, 1.485, 1.51, and 1.53 (72H, 4 × s, *t*-butyl H), 7.73–7.77 (2H, m, quinoxalino H), 7.79 (1H, dd $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.80–7.84 (3H, m, quinoxalino H and C(4′)H), 7.83 (1H, dd $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.93 (2H, dd $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4′)H), 7.95 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 7.96–7.97 (4H, m, C(2′)H and C(6′)H), 8.05 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.68 (1H, s, C(13)H), 8.91 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 8.93 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 9.03 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 9.05 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1$ Hz, β-pyrrolic H); m/z (ESI-TOF) 1199.6 (MH$^+$, 100%); $C_{82}H_{95}ClN_6H^+$ requires 1199.7 (MH$^+$); R_f (light petroleum–dichloromethane; 5 : 1) = 0.30.

2,12/13-Dichloro-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin 5

A solution of iodine monochloride in dichloromethane solution (1 M, 0.72 cm^3, 0.72 mmol) was added to a refluxing solution of 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin **4** (310 mg, 0.29 mmol) in chloroform (30 cm^3). After 2 h a further aliquot of iodine monochloride in dichloromethane (1 M, 0.72 cm^3, 0.72 mmol) was added. The reaction mixture was heated at reflux for a further 2 h and was then allowed to cool to room temperature. Saturated aqueous sodium thiosulfate (100 cm^3) was added and the organic layer was separated. The organic layer was washed with saturated aqueous sodium thiosulfate solution (100 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent was removed. The residue was purified by column chromatography over silica using a dichloromethane : light petroleum mixture (1 : 6) as eluent to give **5** (190 mg, 58%) and **4** (35 mg, 11%). **5**: purple solid, mp >280 °C; found: C, 80.7%; H, 8.25%; N, 4.9%; $C_{76}H_{92}Cl_2N_4$ requires C, 80.6%; H, 8.2%; N, 4.95%; λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 424 (5.56), 490sh (3.60), 520 (4.00), 556 (3.72), 595 (3.71), 651 (3.79); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.94 (2H, br s, NH), 1.49 (36H, m, *t*-butyl H), 1.515 and 1.52 (36H, 2 × s, *t*-butyl H), 7.77 (2H, dd, $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.80 (2H, dd, $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4′)H), 7.91 (4H, m, C(2′)H and C(6′)H), 8.02 (4H, m, C(2′)H and

C(6′)H), 8.69 and 8.70 (2H, 2 × s, C(3)H and C(12)H/C(13)H), 8.84 and 8.91, and 8.87 (4H, comprised of 2 × br s {8.84 and 8.91} and a tight ABq {8.87}, β-pyrrolic H); *m/z* (ESI-TOF) 1131.7 (98%), 1132.7 (81%), 1133.7 (100%), 1134.7 (55%), 1135.7 (27%), 1136.7 (11%), 1137.7 (4%); $C_{76}H_{92}Cl_2N_4H^+$ (MH^+) requires 1131.7 (100%), 1132.7 (85%), 1133.7 (99%), 1134.7 (64%), 1135.7 (35%), 1136.7 (15%), 1137.7 (5%); R_f (light petroleum–dichloromethane; 5 : 1) = 0.33. **4**: a sample co-chromatographed with and had an identical ^{1}H NMR to an authentic sample.

12-Acetoxy-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin 3

To a solution of 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)-quinoxalino[2,3-*b*]porphyrin **1** (100 mg, 0.086 mmol) in chloroform (10 cm^3) were added silver acetate (50 mg, 0.30 mmol) and iodine (50 mg, 0.20 mmol). The reaction mixture was stirred at room temperature in the dark under argon for 1.5 h and then filtered through a short plug of silica using dichloromethane as the eluent. The filtrate was collected, the solvent was removed and the residue was purified by column chromatography over silica using a dichloromethane : light petroleum mixture (gradient from 1 : 6 to 1 : 2) as eluent to give 12-iodo-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin (6.0 mg, 5%), **1** (44 mg, 44%) and **3** (34 mg, 32%). 12-Iodo-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrin: dark purple solid, mp >280 °C; found: C, 76.2%; H, 7.4%; N, 6.4%; $C_{82}H_{95}IN_6$ requires C, 76.3%; H, 7.4%; N, 6.5%); λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 296 (4.28), 344sh (4.37), 364sh (4.42), 413sh (5.03), 438 (5.31), 532 (4.32), 600 (4.01), 655 (2.98); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.70 (1H, br s, NH), −2.54 (1H, br s, NH), 1.48, 1.485, 1.53, and 1.54 (72H, 4 × s, *t*-butyl H), 7.73–7.77 (2H, m, quinoxalino H), 7.81–7.84 (4H, m, quinoxalino H and C(4′)H), 7.92 (2H, dd, $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.95 (4H, m, C(2′)H and C(6′)H), 7.97 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 8.07 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 8.93 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 8.95 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 9.01 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 9.05 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 9.14 (1H, s, C(13)H); *m/z* (ESI-TOF) 1291.5 (MH^+, 100%); $C_{82}H_{95}N_6IH^+$ requires 1291.7 (MH^+); R_f (light petroleum–dichloromethane; 5 : 1) = 0.25. **1**: a sample co-chromatographed with and had an identical ^{1}H NMR to an authentic sample. **3**: orange–brown solid, mp >280 °C; found: C, 82.4%; H, 8.1%; N, 6.85%; $C_{84}H_{98}N_6O_2$ requires C, 82.45%; H, 8.1%; N, 6.9%; ν_{max} (KBr)/cm^{-1} 1766 (C=O); λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 294 (4.36), 339sh (4.40), 356 (4.45), 433 (5.35), 529 (4.28), 562 (3.74), 598 (4.00), 650 (2.97); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.67 (1H, br s, NH), −2.61 (1H, br s, NH), 1.48, 1.49, 1.52, and 1.54 (72H, 4 × s, *t*-butyl H), 1.79 (3H, s, CH_3COO), 7.72–7.76 (2H, m, quinoxalino H), 7.80–7.85 (4H, m, C(4′)H and quinoxalino H), 7.92–7.94 (2H, m, C(4′)H), 7.96 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 7.98 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.00 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 8.11 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 8.52 (1H, s, C(13)H), 8.72 and 9.01 (2H, ABq, $J_{A,B} = 4.5$ Hz, β-pyrrolic H), 8.95 and 9.06 (2H, ABq, $J_{A,B} = 4.5$ Hz, β-pyrrolic H); *m/z* (ESI-TOF) 1223.8216 (100%), 1224.8205 (93%), 1225.8266 (39%), 1226.8217 (11%), 1227.8259 (3%); $C_{84}H_{98}N_6O_2H^+$ (MH^+) requires 1223.7824 (100%), 1224.7856 (94%), 1225.7889 (44%), 1226.7921 (14%), 1227.7952 (3%); R_f (light petroleum–dichloromethane; 2 : 1) = 0.24.

2-Acetoxy-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin 8

To a solution of 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)-porphyrin **4** (6.70 g, 6.30 mmol) in chloroform (420 cm^3) were added silver acetate (3.00 g, 18.0 mmol) and iodine (3.00 g, 11.8 mmol). The reaction mixture was stirred at room temperature in the dark under argon for 1.5 h and then filtered through a short plug of silica gel using dichloromethane as the eluent. The filtrate was collected and the solvent was removed, and the residue was purified by column chromatography over silica using a dichloromethane : light petroleum (gradient from 1 : 6 to 1 : 1) as eluent to give **9** (0.48 g, 6%), **4** (2.38 g, 36%), **8** (2.62 g, 37%) and **10** (0.31 g, 5%). **9**: red solid, mp >280 °C; found: C, 76.8%; H, 7.8%; N, 4.6%; $C_{76}H_{93}IN_4$ requires C, 76.7%; H, 7.9%; N, 4.7%; λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 303 (4.19), 369sh (4.40), 424 (5.67), 489 (3.61), 520 (4.35), 556 (3.92), 595 (3.79), 651 (3.85); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.75 (2H, br s, NH), 1.52, 1.525, 1.53, and 1.54 (72H, 4 × s, *t*-butyl H), 7.80 (2H, dd, $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.82 (1H, dd, $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.83 (1H, dd, $J_{2',4'} = J_{6',4'} = 2$ Hz, C(4′)H), 7.94 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 8.06 (2H, d, $J_{4',2'} = J_{4',6'} = 2$ Hz, C(2′)H and C(6′)H), 8.07–8.09 (4H, m, C(2′)H and C(6′)H), 8.82 and 8.84 (2H, ABq, $J_{A,B} = 4$ Hz, β-pyrrolic H), 8.89–8.92 (3H, m, β-pyrrolic H), 8.96 (1H, 1/2ABq, $J_{A,B} = 5$ Hz, β-pyrrolic H), 9.21 (1H, s, C(3)H); *m/z* (ESI) 1189.6 (100%); $C_{76}H_{93}IN_4H^+$ (MH^+) requires 1189.6 (100%); R_f (light petroleum–dichloromethane; 5 : 1) = 0.26. **4**: a sample co-chromatographed with and had an identical ^{1}H NMR to an authentic sample. **8**: red solid, mp >280 °C; found: C, 83.6%; H, 8.7%; N, 4.9%; $C_{78}H_{96}N_4O_2$ requires C, 83.5%; H, 8.6%; N, 5.0%; ν_{max} (KBr)/cm^{-1} 1767 (C=O); λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 304 (3.86), 327sh (3.81), 371sh (4.05), 421 (5.34), 486 (3.26), 517 (3.95), 553 (3.61), 591 (3.42), 647 (3.38); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.77 (2H, br s, NH), 1.53 (18H, s, *t*-butyl H), 1.54 (18H, s, *t*-butyl H), 1.55 (36H, s, *t*-butyl H), 1.82 (3H, s, CH_3COO), 7.80 (4H, br m, C(4′)H), 8.00 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.09 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.10 (4H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.61 (1H, s, C(3)H), 8.68 and 8.90 (2H, ABq, $J_{A,B} = 5$ Hz, β-pyrrolic H), 8.84 and 8.86 (2H, tight ABq, $J_{A,B} = 5$ Hz, β-pyrrolic H), 8.92 and 8.95 (2H, ABq, $J_{A,B} = 5$ Hz, β-pyrrolic H); *m/z* (ESI-TOF) 1121.7546 (100%), 1122.7572 (86%), 1123.7642 (32%), 1124.7635 (8%), 1125.7638 (2%); $C_{78}H_{96}N_4O_2H^+$ (MH^+) requires 1121.7606 (100%), 1122.7639 (87%), 1123.7672 (38%), 1124.7704 (11%), and 1125.7736 (2%); R_f (light petroleum–dichloromethane; 2 : 1) = 0.27. **10**: red solid, mp >280 °C; found: C, 81.5%; H, 8.3%; N, 4.7%; $C_{80}H_{98}N_4O_4$ requires C, 81.45%; H, 8.4%; N, 4.75%; ν_{max} (KBr)/cm^{-1} 1768 (C=O); λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 307 (4.27), 379sh (4.44), 402sh (5.04), 421 (5.69), 489sh (3.67), 518 (4.38), 553 (3.96), 590 (3.87), 645 (3.77); ^{1}H NMR (500.3 MHz; CD_2Cl_2) δ: −2.93 (2H, br s, NH), 1.50, 1.51, 1.52 and 1.53 (72H, 4 × s, *t*-butyl H), 1.78 (6H, s, CH_3COO), 7.77–7.78 (4H, m, C(4′)H), 7.95–7.97 (4H, m, C(2′)H and C(6′)H), 8.06–8.08 (4H, m, C(2′)H and C(6′)H), 8.53 and 8.55 (2H, 2 × s, C(3)H and C(12)H or C(13)H), 8.63 (1H, br s, β-pyrrolic H), 8.67

and 8.87 (2H, ABq, $J_{A,B} = 5$ Hz, β-pyrrolic H), 8.92 (1H, br s, β-pyrrolic H); *m/z* (ESI) 1179.6 (100%); $C_{80}H_{98}N_4O_4H^+$ (MH^+) requires 1179.8 (100%); R_f (light petroleum–dichloromethane; 1 : 1) = 0.34.

12,13-Dioxo-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)chlorin 13

Potassium carbonate (100 mg, 0.72 mmol) was added to a solution of **8** (95 mg, 0.088 mmol) in a dichloromethane : methanol mixture (1 : 1) (18 cm^3) under argon. The suspension was stirred at room temperature in the dark for 6 h. Ether (20 cm^3) and water (10 cm^3) were added to the reaction mixture. The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and the solvent was removed. Dess–Martin periodinane (DMP) (37 mg, 0.088 mmol) was added to a solution of the crude 2-hydroxy-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin in dichloromethane (15 cm^3). The reaction mixture was stirred at room temperature in the dark under argon for 1 h before a second aliquot of DMP (37 mg, 0.088 mmol) was added. The reaction mixture was stirred for a further 0.5 h and then filtered through a plug of silica gel using dichloromethane as the eluent. The filtrate was collected and the solvent was removed. The residue was purified by preparative thin layer chromatography using a dichloromethane : light petroleum mixture (1 : 2) as eluent to give **13** (67 mg, 72%), a sample of which co-chromatographed with [R_f (light petroleum–dichloromethane; 2 : 1) = 0.17] and had an identical ^{1}H NMR to an authentic sample.[19]

2-Acetoxy-12,13-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin 14

To a solution of **13** (50 mg, 0.046 mmol) in a chloroform : acetic acid mixture (1 : 1) (10 cm^3) were added silver acetate (26 mg, 0.16 mmol) and iodine (26 mg, 0.10 mmol). The reaction mixture was stirred at room temperature in the dark under argon for 4 h and then poured into a saturated aqueous sodium bicarbonate solution (30 cm^3). Solid sodium bicarbonate was added until the pH = 8. The aqueous layer was extracted with dichloromethane (3 × 5 cm^3). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and then the solvent was removed. The residue was purified by column chromatography over silica using a dichloromethane : light petroleum mixture (gradient from 1 : 3 to 2 : 3) as eluent to give **14** (24 mg, 46%) and the starting material **8** (9 mg, 18%). **14**: green solid, mp >280 °C; found: C, 81.2%; H, 8.1%; N, 4.8%; $C_{78}H_{94}N_4O_4$ requires C, 81.35%; H, 8.2%; N, 4.9%; ν_{max} (KBr)/cm^{-1} 1767 (C=O), 1728 (C=O); λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 389sh (5.06), 406 (5.32), 475 (4.35), 546sh (3.84), 613 (3.76), 673sh (3.70), 709sh (3.68), 781 (3.25); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.13 (1H, br s, NH), −2.06 (1H, br s, NH), 1.48, 1.485, 1.50, and 1.52 (72H, 4 × s, *t*-butyl H), 1.76 (3H, s, CH_3COO), 7.71 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 7.72 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 7.74 (2H, dd, $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4′)H), 7.75 (2H, dd, $J_{2',4'} = J_{6',4'} = 1.5$ Hz, C(4′)H), 7.90 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.00 (2H, d, $J_{4',2'} = J_{4',6'} = 1.5$ Hz, C(2′)H and C(6′)H), 8.37 (1H, s, C(3)H), 8.53 (1H, dd, $J_{\beta,\beta} = 5.0$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 8.56 (1H, dd, $J_{\beta,\beta} = 5$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 8.62 (1H, dd, $J_{\beta,\beta} = 5.0$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H), 8.77 (1H, dd, $J_{\beta,\beta} = 5.0$ Hz, $J_{NH,\beta} = 1.5$ Hz, β-pyrrolic H); *m/z* (ESI-TOF) 1151.8 (100%), 1152.8 (75%), 1153.8 (27%), 1154.8 (8%); $C_{78}H_{94}N_4O_4H^+$ (MH^+) requires 1151.7 (100%), 1152.7 (90%), 1153.7 (41%), 1154.7 (12%); R_f (light petroleum–dichloromethane; 2 : 1) = 0.13. **8**: a sample co-chromatographed with and had an identical ^{1}H NMR to an authentic sample.

2,3,12,13-Tetraoxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)bacteriochlorin 15

Method (i) *via* compound 10. Potassium carbonate (50 mg, 0.36 mmol) was added to a solution of **10** (50 mg, 0.042 mmol) in a dichloromethane : methanol mixture (1 : 1) (14 cm^3) under argon. The suspension was stirred at room temperature in the dark for 6 h. Ether (10 cm^3) and water (10 cm^3) were added to the reaction mixture. The organic layer was separated, dried over anhydrous sodium sulfate and filtered. The solvent was removed and the crude 2,12/13-dihydroxy-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin was dissolved in dichloromethane (15 cm^3). DMP (36 mg, 0.085 mmol) was added and the reaction mixture was stirred at room temperature in the dark under argon for 1 h. Another portion of DMP (36 mg, 0.085 mmol) was then added and the reaction mixture was stirred for a further 0.5 h. The reaction mixture was then filtered through a plug of silica using dichloromethane as the eluent. The filtrate was collected and the solvent was removed. The residue was purified by preparative thin layer chromatography using a dichloromethane : light petroleum mixture (1 : 2) as eluent to give **15** (22 mg, 47%), a sample of which co-chromatographed with [R_f (light petroleum–dichloromethane; 1 : 1) = 0.42] and had an identical ^{1}H NMR to the authentic sample.[20]

Method (ii) *via* compound 14. Potassium carbonate (25 mg, 0.18 mmol) was added to a solution of **14** (25 mg, 0.022 mmol) in a dichloromethane : methanol mixture (1 : 1) (10 cm^3) under argon. The suspension was stirred at room temperature in the dark for 6 h. Ether (10 cm^3) and water (5 cm^3) were added and the organic layer was separated, dried over anhydrous sodium sulfate, and filtered. The solvent was removed and the crude 2-hydroxy-12,13-dioxo-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)chlorin was dissolved in dichloromethane (2 cm^3). DMP (9.0 mg, 0.022 mmol) was added and the reaction mixture was stirred at room temperature in the dark under argon for 0.5 h. Another portion of DMP (9.0 mg, 0.022 mmol) was added and the reaction mixture was stirred for a further 0.5 h. The mixture was filtered through a plug of silica using dichloromethane as the eluent. The filtrate was collected, the solvent was removed, and the residue was purified by preparative thin layer chromatography using a dichloromethane : light petroleum mixture (1 : 2) as eluent to give **15** (10 mg, 41%), a sample of which co-chromatographed with and had an identical ^{1}H NMR to an authentic sample.[20]

2,12/13-Dichloro-5,10,15,20-tetraphenylporphyrin 7

A solution of iodine monochloride in dichloromethane (1 M, 0.41 cm^3, 0.41 mmol) was added to a solution of 5,10,15,20-tetraphenylporphyrin **6** (100 mg, 0.16 mmol) in chloroform (10 cm^3) heated at reflux. After 2 h a further aliquot of iodine monochloride in dichloromethane (1 M, 0.41 cm^3, 0.41 mmol) was

added. The reaction mixture was heated at reflux for a further 2 h and was then allowed to cool to room temperature. Saturated aqueous sodium thiosulfate (20 cm^3) was added and the organic layer was separated. The organic layer was washed with saturated aqueous sodium thiosulfate solution (20 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent was removed. The residue was purified by column chromatography over silica using a chloroform : light petroleum mixture (from 1 : 3 to 1 : 2) as eluent to give **7** (51 mg, 46%) and **4** (23 mg, 23%). **7**: purple solid, mp >300 °C; found: C, 77.2%; H, 4.1%; N, 8.2%; $C_{44}H_{28}Cl_2N_4$ requires C, 77.3%; H, 4.1%; N, 8.2%; λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 269 (4.10), 313 (4.11), 371sh (4.49), 421 (5.49), 488sh (3.48), 519 (4.29), 553 (3.61), 593 (3.71), 649 (3.72); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.96 (2H, br s, NH), 7.71–7.82 (12H, m, *meso*-phenyl H), 8.08–8.10 (4H, m, *meso*-phenyl H), 8.17–8.20 (4H, m, *meso*-phenyl H), 8.66 and 8.67 (2H, 2 × s, C(3)H and C(12)H/C(13)H), 8.78 and 8.91, and 8.82 and 8.85 (4H, comprised of 2 × br s {8.78 and 8.91} and a tight ABq {8.82 and 8.85}, $J_{A,B}$ = 5 Hz, β-pyrrolic H); *m*/*z* (ESI-TOF) 683.2 (100%); $C_{44}H_{28}Cl_2N_4H^+$ (MH^+) requires 683.7 (100%); R_f (light petroleum–dichloromethane; 2 : 1) = 0.21. **4**: a sample co-chromatographed with and had an identical ^{1}H NMR to an authentic sample.

2-Acetoxy-5,10,15,20-tetraphenylporphyrin 11

To a solution of 5,10,15,20-tetraphenylporphyrin **6** (100 mg, 0.16 mmol) in chloroform (10 cm^3) were added silver acetate (50 mg, 0.30 mmol) and iodine (50 mg, 0.20 mmol). The reaction mixture was stirred at room temperature in the dark under argon for 1.5 h and was then treated with a further aliquot of silver acetate (50 mg, 0.30 mmol) and iodine (50 mg, 0.20 mmol). Half an hour later, the mixture was filtered through a short plug of silica gel using dichloromethane as the eluent. The filtrate was collected, the solvent was removed, and the residue was purified by column chromatography over silica using a chloroform : light petroleum (gradient from 1 : 2 to 2 : 1) as eluent to give **12** (6 mg, 5%), **6** (43 mg, 43%) and **11** (35 mg, 32%). **12**: purple solid, mp >300 °C; found: C, 71.3%; H, 4.0%; N, 7.7%; $C_{44}H_{29}IN_4$ requires C, 71.4%; H, 4.0%; N, 7.6%; λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 250 (4.26), 273 (4.23), 308 (4.38), 403sh (5.06), 421 (5.66), 487 (3.58), 518 (4.38), 552 (3.79), 593 (3.80), 649 (3.74); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.79 (2H, br s, NH), 7.75–7.85 (12H, m, *meso*-phenyl H), 8.11–8.13 (2H, m, *meso*-phenyl H), 8.21–8.24 (6H, m, *meso*-phenyl H), 8.77 and 8.79 (2H, tight ABq, $J_{A,B}$ = 5 Hz, β-pyrrolic H), 8.84 and 8.86 (2H, tight ABq, $J_{A,B}$ = 5 Hz, β-pyrrolic H), 8.90 and 8.92 (2H, tight ABq, $J_{A,B}$ = 5 Hz, β-pyrrolic H), 9.16 (1H, s, C(3)H); *m*/*z* (ESI-TOF) 741.1 (100%); $C_{44}H_{29}IN_4H^+$ (MH^+) requires 741.2 (100%); R_f (light petroleum–dichloromethane; 2 : 1) = 0.14. **6**: a sample co-chromatographed with and had an identical ^{1}H NMR to an authentic sample. **11**: purple solid, mp >300 °C; found: C, 82.0%; H, 4.7%; N, 8.2%; $C_{46}H_{32}N_4O_2$ requires C, 82.1%; H, 4.8%; N, 8.3%; ν_{max} (KBr)/cm^{-1} 1755 (C=O); λ_{max} (CH_2Cl_2)/nm (log(ε/dm^{-3} mol^{-1} cm^{-1})) 249 (4.17), 273 (4.15), 306 (4.15), 374sh (4.48), 417 (5.64), 484 (3.53), 514 (4.30), 549 (3.82), 589 (3.77), 644 (3.57); ^{1}H NMR (400.1 MHz; $CDCl_3$) δ: −2.83 (2H, br s, NH), 1.87 (3H, s, CH_3COO), 7.75–7.79 (12H, m, *meso*-phenyl H), 8.14–8.16 (2H, m, *meso*-phenyl H), 8.22–8.25 (6H, m, *meso*-phenyl H), 8.58 (1H, s, C(3)H), 8.71 and 8.87 (2H, ABq, $J_{A,B}$ = 5 Hz, β-pyrrolic H), 8.81 and 8.82 (2H, tight ABq, $J_{A,B}$ = 5 Hz, β-pyrrolic H), 8.89 and 8.92 (2H, ABq, $J_{A,B}$ = 5 Hz, β-pyrrolic H); *m*/*z* (ESI-TOF) 673.2 (100%); $C_{46}H_{32}N_4O_2H^+$ (MH^+) requires 673.8 (100%); R_f (light petroleum–dichloromethane; 2 : 3) = 0.16.

Conclusion

In conclusion we have shown that pseudohalogens can be used to regiospecifically introduce functional groups onto the porphyrin β-pyrrolic positions. The mechanism of addition most likely occurs *via* a single electron transfer process and can be used to attach chloro, nitro and acetoxy groups. The acetoxylation procedure gives a new simple methodology for the preparation of chlorin-α-diones and bacteriochlorin-tetraones in good yield.

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