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Bacteriopurpurins: Synthesis from *meso*-Diacrylate Substituted Porphyrins

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Abstract—A new route to the synthesis of bacteriopurpurins from symmetrical and unsymmetrical *meso*-substituted diacrylate octaalkylporphyrins has been achieved using basic conditions. Reaction of 5,15-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin or 5,15-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I, in toluene in the presence of DBU, produces the corresponding bacteriopurpurins, without formation of the corresponding iso-bacteriopurpurins. Bacteriopurpurin formation from the cyclization of the 5,10-bis[β-(ethoxycarbonyl)-vinyl]porphyrins were found to be dependent on the initial cyclization process and the structure of the *meso*-acrylate purpurin formed. In the etioporphyrin series the cyclization process was shown to be highly specific, favoring cyclization of the acrylate groups toward a specific ethyl group on the porphyrin ring.

Background

A large number of naturally occurring and synthetic porphyrin derivatives are currently being evaluated with potential application to the fields of artificial photosynthesis[1] and photodynamic therapy.[2] Chlorins and purpurins are a subclass of porphyrins in which one of the pyrrole rings of the porphyrin macrocycle has been reduced. In particular, purpurins possess an annelated cyclopentenyl ring attached directly to the reduced pyrrole ring (Fig. 1). Bacteriochlorins[3] and *iso*-bacteriochlorins are a subclass of porphyrins in which two of the pyrrole rings of the macrocycle have been reduced. Bacteriochlorins have opposing pyrrole rings reduced while *iso*-bacteriochlorins have adjacent pyrrole rings reduced (Fig. 1).

Reduction of the pyrrolic rings in the porphyrin macrocycle has a pronounced effect on the absorption spectra of the reduced compound. Bacteriochlorins have large band I (or Qy) absorptions that absorb in the region 720–830 nm. The position of the band I absorption is largely dependent on the functional groups directly attached to the tetrapyrrolic ring system.

The synthesis of bacteriochlorins from chlorins or porphyrins is not a trivial exercise of chemistry. A relatively small number of synthetic bacteriochlorin analogues have been made.[3] The cyclization of bis-acrylate octaethylporphyrins under acidic conditions (AcOH, N_2) was attempted by Morgan and coworkers,[4] in an attempt to produce *iso*-bacterio or bacteriopurpurins, with no success. In our

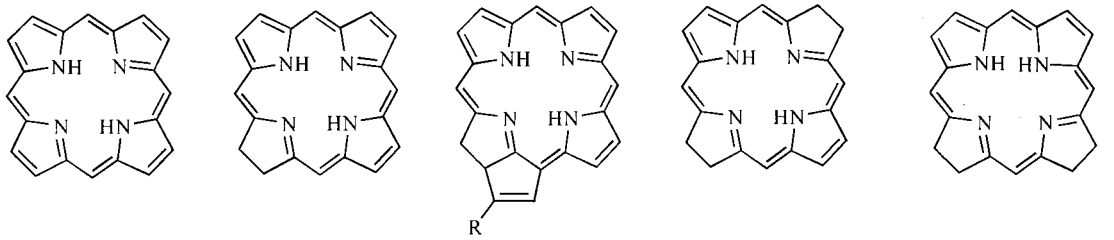

Figure 1.

Keywords: bacteriopurpurins; porphyrin; cyclization.

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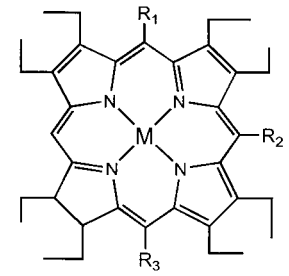
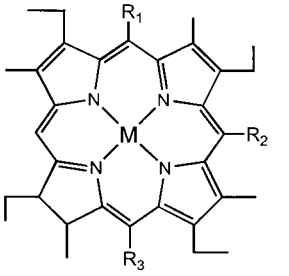


(1) M = Ni (II), R_1= CHO, R_2 = CH=CHCO$_2$Et, R_3 = H
(2) M = Ni (II), R_1= CHO, R_2 = H, R_3= CHCHCO$_2$Et
(3) M = Ni (II), R_1= R_3 = CHCHCO$_2$Et, R_2 = H
(4) M = Ni (II), R_1= R_2 = CHCHCO$_2$Et, R_3 = H
(5) M = H2, R_1= R_2 = CHCHCO$_2$Et, R_3 = H
(6) M = H2, R_1= R_3 = CHCHCO$_2$Et, R_2 = H

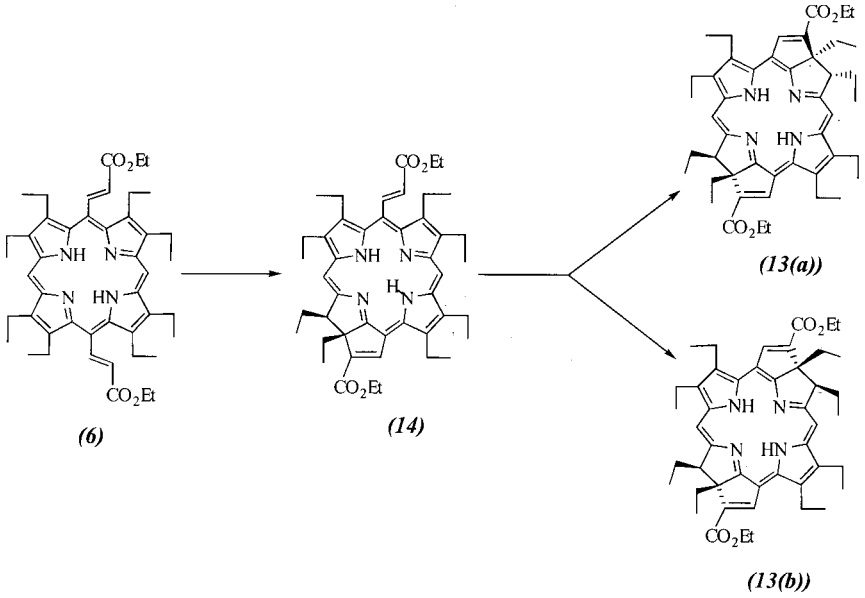


(7) M = Ni (II), R_1= CHO, R_2 = CHO, R_3 = H
(8) M = Ni (II), R_1= CHO, R_2 = H, R_3 = CHO
(9) M = Ni (II), R_1= R_2 =CHCHCO$_2$Et, R_3 = H
(10) M = Ni (II), R_1= R_3 =CHCHCO$_2$Et, R_2 = H
(11) M = H2, R_1= R_2 =CHCHCO$_2$Et, R_3 = H
(12) M = H2, R_1= R_3 =CHCHCO$_2$Et, R_2 = H

Figure 2.

studies on the mechanisms of cyclization of *meso*-acrylate porphyrins, we have demonstrated that a variety of bases efficiently convert *meso*-acrylate porphyrins into purpurins.[5,6] Based on these results, cyclization of bis-acrylate porphyrins was attempted using basic catalysis in the hope of generating synthetic bacteriopurpurins with long wavelength absorption. In addition, as the cyclization process in purpurins has been demonstrated to be a mildly selective process, favoring cyclization in general toward an ethyl group for example,[7] we were particularly interested to see if some cyclization selectivity is observed on cyclizing unsymmetrical bis-acrylate porphyrins. For this study we chose to use octaethylporphyrin and etioporphyrin I as starting porphyrins for the synthesis of bacteriopurpurin derivatives.

Using a modification to the method of Morgan and coworkers, Ni (II) 5-formyl-10-[β-(ethoxycarbonyl)vinyl]-octaethylporphyrin (**1**) and Ni (II) 5-formyl-15-[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**2**) were synthesized from Ni (II) 5-[β-(ethoxycarbonyl)vinyl]octaethylporphyrin via Vilsmeier formylation with (chloromethylene)dimethylammonium chloride, at room temperature. After hydrolysis of the resulting iminium salt and chromatography on silica (dichloromethane), a single major green band was isolated. ^{1}H NMR showed that the band was a mixture of the two expected geometric isomers (**1**) and (**2**) in a ratio of ~1:2 as expected statistically. These two isomers were not separated at this stage, but converted directly to the Ni (II) bis-[β-(ethoxycarbonyl)vinyl]porphyrins (**3**) and (**4**) by reaction with (carboethoxymethylene)triphenylphosphorane in DMF



(6) *(14)* *(13(a))* *(13(b))*

Scheme 1.

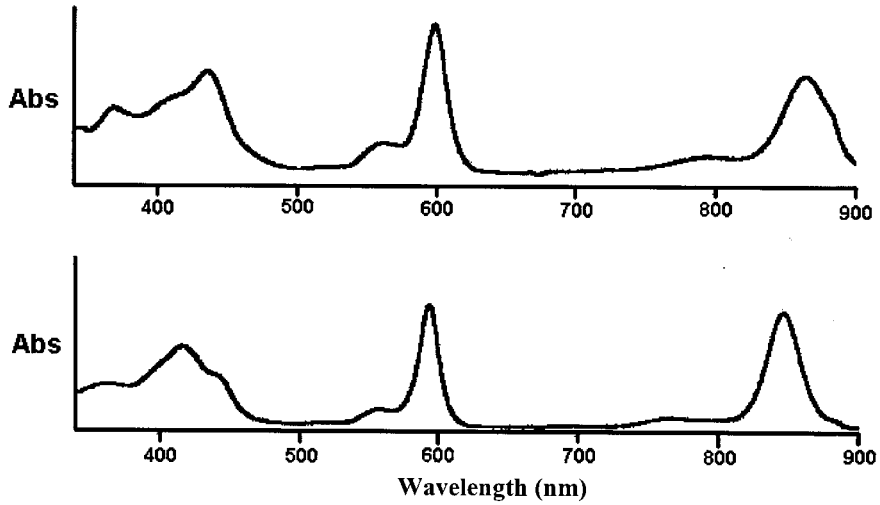
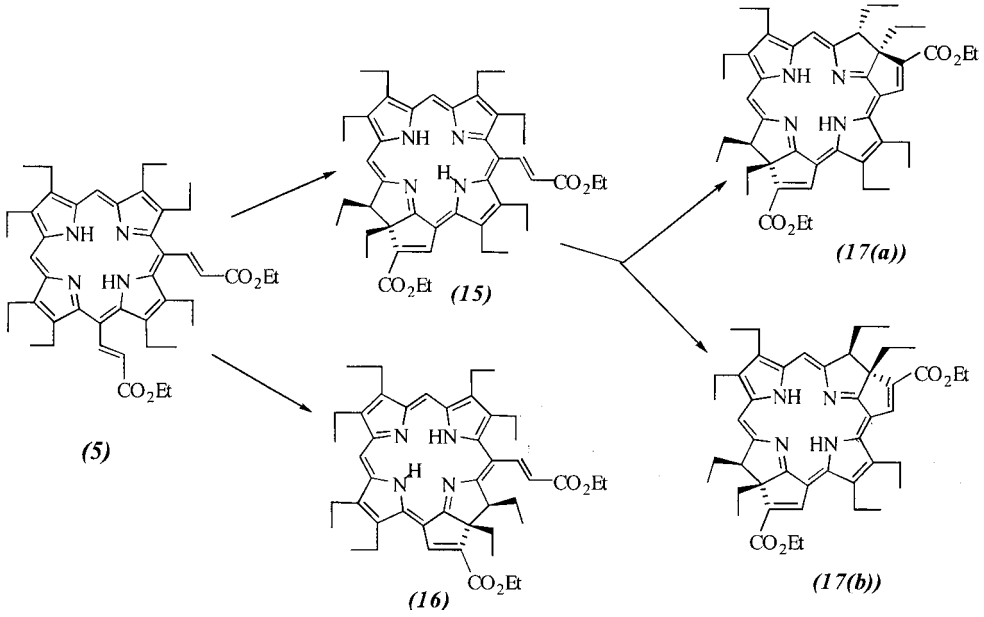


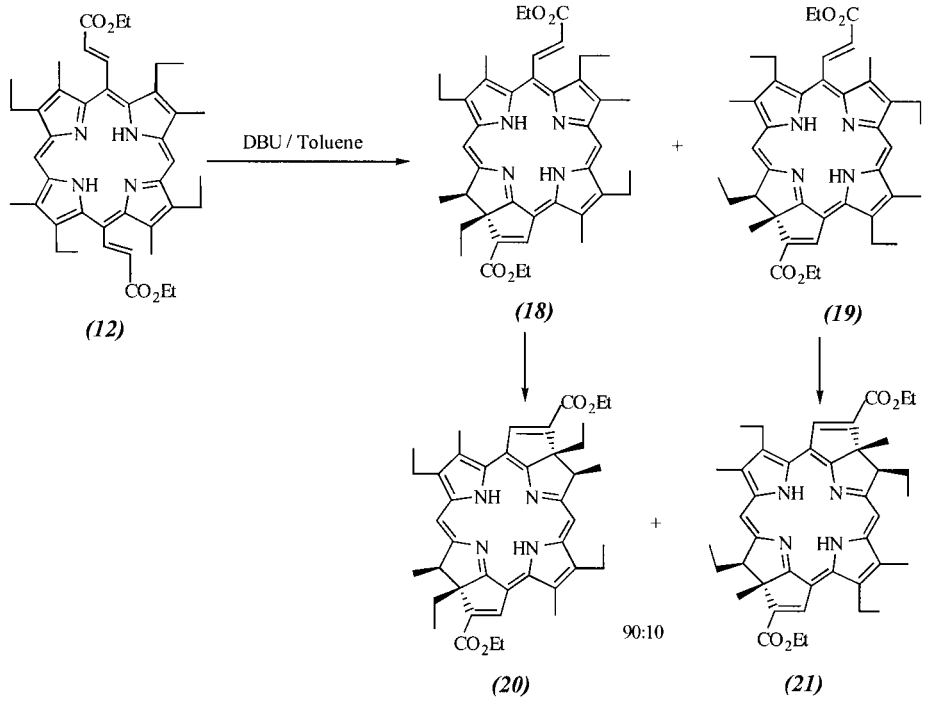
Figure 3. Top: 5,10-etiobacteriopurpurin (**27a,b**) in dichloromethane. Bottom: 5,15-octaethylbacteriopurpurin (**13b**) in dichloromethane.

under a nitrogen atmosphere. Separation of the Ni (II) 5,15-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin and the Ni (II) 5,10-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin was effected by column chromatography using toluene as eluent, the 5,15 isomer being slightly less polar in this solvent system. Each isomer respectively was then demetallated using sulfuric acid/methylene chloride to yield the desired free base diacrylate analogs (**5**) and (**6**) (Fig. 2).

Cyclization of 5,15-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**6**) in refluxing toluene/DBU under an argon atmosphere was complete in approximately 4–6 h, producing the 5,15-octaethylbacteriopurpurins (**13a,b**) almost exclusively in ~70% yield (Scheme 1). A minor polar band was also isolated and this proved to be the 15-[β-(ethoxycarbonyl)vinyl]purpurin (**14**). Close monitoring of the reaction by TLC and UV/visible spectroscopy over the course of the reaction showed that the 15-[β-(ethoxycarbonyl)vinyl]-purpurin (**14**) was rapidly formed initially. This compound displayed a typical purpurin absorption spectra with a band I absorption maxima at 700 nm. The cyclization of the second acrylate group proceeded with equal efficiency to give the desired 5,15-octaethylbacteriopurpurins (**13a,b**). The 5,15-octaethylbacteriopurpurins (**13a,b**) were isolated as a single band from the crude reaction mixture by chromatography on silica. A 500 MHz ^{1}H NMR of the 5,15-octaethylbacteriopurpurin band showed it to be a mixture of the facial isomers (**13a**) and (**13b**) in a ratio of 16:84. The isomers in this instance result from cyclization of the second *meso*-acrylate group (Scheme 1). Depending on the initial orientation of the acrylate group, cyclization of the second acrylate group gives rise to the ethyl groups on the reduced pyrrole rings being either on the same or opposite sides of the porphyrin face. It is interesting to note that no *iso*-bacteriopurpurin formation was observed. Pure facial isomer (**13b**) could be isolated by successive recrystallizations from dichloromethane/methanol. The UV/visible absorption spectra of (**13b**) (Fig. 3, bottom) displays a prominent band I



Scheme 2.



Scheme 3.

absorption at 846 nm, a sharp absorption band at 593 nm and a broad Soret absorption band at 416 nm.

Cyclization of 5,10-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin I (**5**) (Scheme 2) in refluxing toluene/DBU under an argon atmosphere was complete by UV/visible spectroscopy after approximately 24 h. Isolation of the products by chromatography on silica (dichloromethane) gave two major components, 5,10-octaethylbacteriopurpurins (**17a,b**) (50% yield) as a single eluting band and 10-[β-(ethoxycarbonyl)vinyl]octaethylpurpurin (**16**) in a yield of 40%, the latter being crystallized from dichloromethane/methanol. The 5,10-octaethylbacteriopurpurins (**17a**) and (**17b**) could not be separated from each other by silica gel chromatography. Close monitoring of the reaction by TLC and UV/visible spectroscopy over the course of the reaction showed that two *meso*-acrylate purpurins (**15**) and (**16**) are initially rapidly formed, with the *meso*-acrylate purpurin (**15**) further cyclizing slowly to give the desired 5,10-octaethylbacteriopurpurins (**17a,b**). Formation of the 10-[β-(ethoxycarbonyl)vinyl]purpurin (**16**) in approximately equal yield to the 5,10-octaethylbacteriopurpurins (**17a,b**) shows that there is little selectivity in the direction of cyclization of the first *meso*-acrylate group, either away from or toward the pyrrole ring between the two acrylate groups. The 5,10-octaethylbacteriopurpurins (**17a,b**) could not be induced to crystallize and a 500 MHz ^{1}H NMR clearly demonstrated the presence of an equal mixture of two geometric isomers (**17a**) and (**17b**) resulting from cyclization of the second *meso*-acrylate group (Scheme 2). The UV/visible absorption spectra of the 5,10-octaethylbacteriopurpurin mixture is very similar to that of 5,15-octaethylbacteriopurpurin (**13b**), displaying a prominent band I absorption at 863 nm, a sharp absorption band at 598 nm and a broad Soret absorption band at 434 nm.

Cyclization of unsymmetrical *meso*-vinyl substituted porphyrins under various conditions has been shown to be dependent on the pyrrole substituents, the functionality on the *meso*-vinyl group and the cyclization catalyst (acid or base). Cyclization of unsymmetrical bis-acrylate porphyrins using base catalysis was expected to produce some interesting cyclization selectivity and this proved to be the case. 5,15-bis[β-(Ethoxycarbonyl)vinyl]etioporphyrin I (**12**), (produced via a Wittig reaction on the 5,15-diformyl Ni (II) etioporphyrin (**8**) and subsequent demetallation), after refluxing for 6 h in the presence of DBU in toluene, cyclized rapidly to give four products by TLC. Analysis of the mixture by TLC showed two close running bright green fractions, and two brown green bands. The two bright green bands could only be isolated as a single band by chromatography on silica using dichloromethane as eluent. Subsequent analysis of the band by ^{1}H NMR (500 MHz) showed the band to be a mixture of the

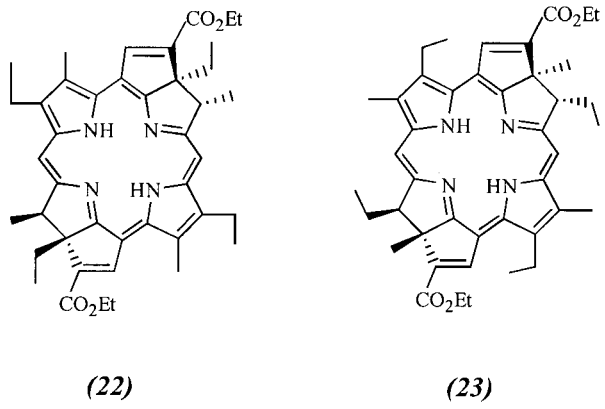
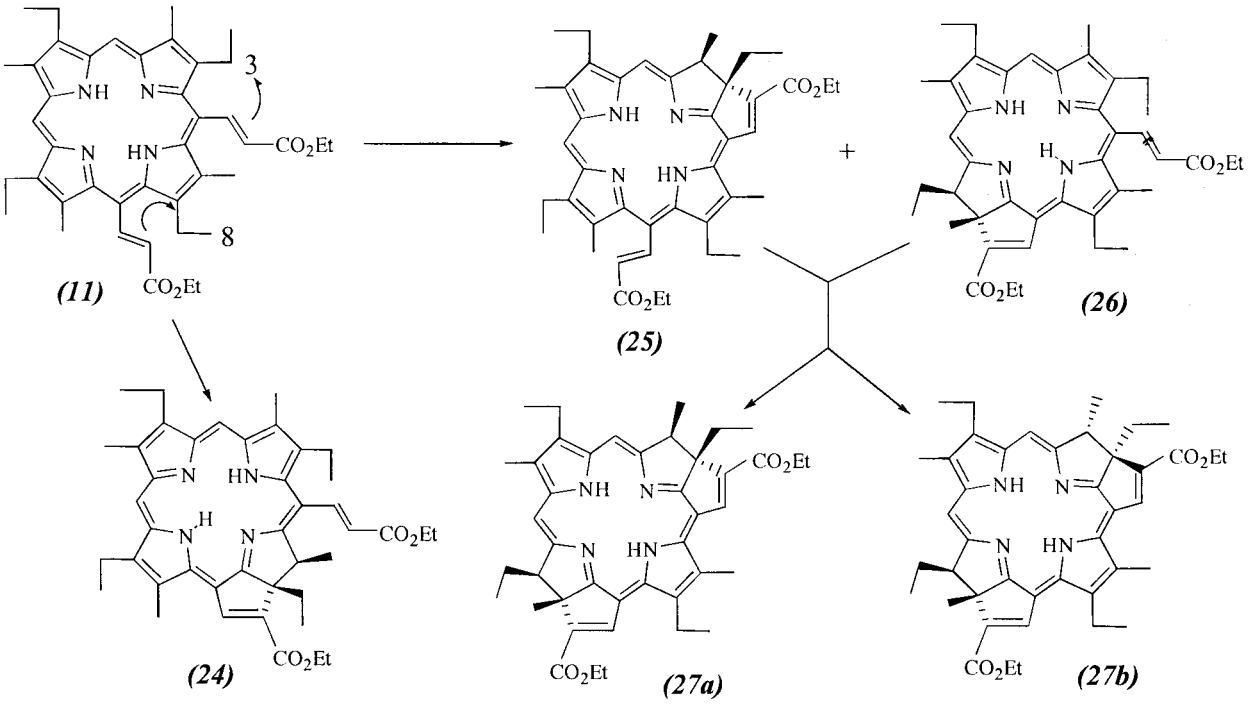


Figure 4.



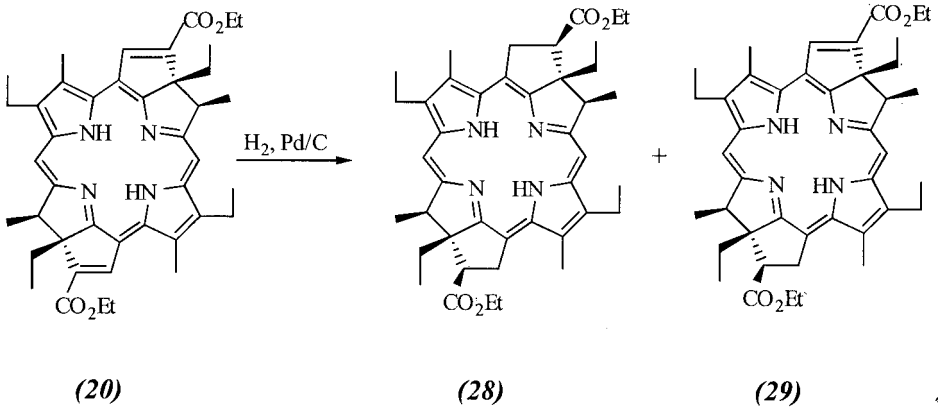
Scheme 4.

5,15-bacterioetiopurpurin isomers (**20**) and (**21**) in a ratio of 90:10 (Scheme 3). A single recrystallization of the crude product from methanol gave pure facial isomer (**20**).

5,15-Bacterioetiopurpurin (**21**) was isolated from the methanol mother liquors and recrystallized from dichloromethane/hexane. The stereochemistry of the facial isomer (**20**) was proven by X-ray crystallography[8] and while we have not achieved a crystal structure of (**21**) it is assumed that the bacteriopurpurin (**21**) behaves similarly to that of (**20**) with regard to the orientation of the alkyl groups on the reduced pyrrole rings. No formation of the facial isomer bacteriopurpurins (**22**) and (**23**) (Fig. 4) were observed by NMR or could be isolated.

Isolation of the two minor remaining purpurin fractions of the reaction was achieved by chromatography on silica using dichloromethane as eluent. The fastest running band was identified as the 15-[β-(ethoxycarbonyl)vinyl]purpurin (**18**), while the second was characterized as the 15-[β-(ethoxycarbonyl)vinyl]purpurin (**19**). Thus the initial acrylate cyclization of the diacrylate porphyrin (**12**) does proceed in the direction of both the ethyl and methyl groups adjacent to the acrylate group, but largely favors cyclization toward the ethyl group.

The geometric selectivity in the acrylate cyclization process toward the ethyl groups on the pyrrole rings was again observed for the cyclization of the 5,10-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin derivative (**11**) under the same reaction conditions (Scheme 4). By TLC and UV/vis spectroscopy, (**11**) is rapidly transformed to purpurin derivatives in 2–3 h. After 24 h at reflux, TLC (dichloromethane) showed the formation of a major green/brown purpurin band and a minor, less polar, intense green bacteriopurpurin band. Isolation of the bands by chromatography on silica and subsequent analysis by 500 MHz ^{1}H NMR showed that the minor band component (15%) was the



Scheme 5.

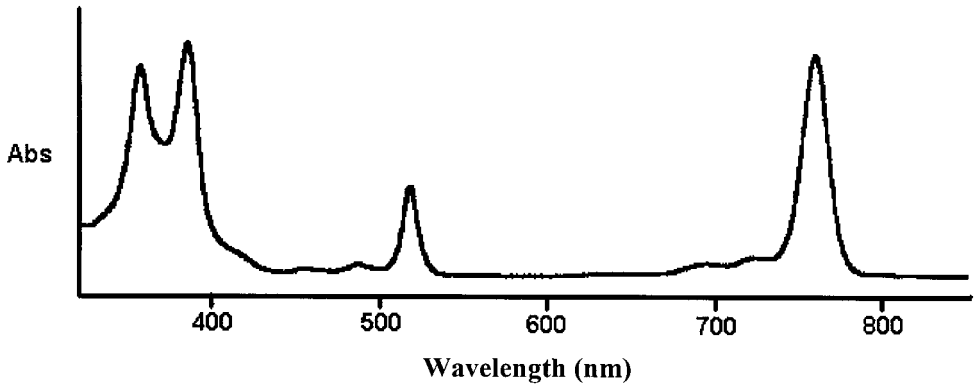


Figure 5. UV/Visible absorption spectra of (**28**) in dichloromethane.

5,10-bacterioetiopurpurins (**27a,b**) being an equal mixture of the two possible cyclization facial isomers. The major brown band consisted of the 10-bis[β-(ethoxycarbonyl)-vinyl]purpurin (**24**). Purification of purpurin (**24**) was achieved easily by crystallization from dichloromethane/methanol (yield 70%). In this instance, cyclization of the 10-acrylate group adjacent to the ethyl group on the eighth carbon position is almost totally favored over cyclization of the 5-acrylate group toward the ethyl group in the third carbon position (Scheme 4). The 20-[β-(ethoxycarbonyl)-vinyl]purpurin (**26**) is able to be isolated as a very minor band from the reaction mixture if the reaction is stopped prior to completion. One cannot totally rule out the possibility of 20-[β-(ethoxycarbonyl)vinyl]purpurin (**26**) playing some role in the formation of bacteriochlorin (**27a,b**), however it is more likely that purpurin (**25**) is the major intermediate in the synthesis of the 5,10-bacterioetiopurpurins (**27a,b**).

Hydrogenation of Bacteriopurpurins

The hydrogenation of the 5-membered isocyclic ring double bond in purpurins has previously been reported in the literature.[7] Hydrogenation has been shown to occur on the side of the ring opposite to the angular alkyl group on the reduced pyrrole ring.[9] Hydrogenation of the 5,15-bacterioetiopurpurin (**20**) in THF with $Pd/C/H_2$ proceeds smoothly to give the tetrahydro-bacterioetiopurpurin (**28**) (Scheme 5) in 90% yield. The UV/visible absorption spectra of (**28**) shows a strong band I absorption at 761 nm and several smaller Q band absorptions at 725, 696, 517, 487, 454 nm. Interestingly the Soret is split with absorptions at 385 and 357 nm (Fig. 5). If the hydrogenation reaction is stopped before completion and analyzed by UV/visible spectroscopy, a band absorbing at 806 nm is clearly observable. This is most likely the mono-hydrogenated bacteriopurpurin (**29**) (Scheme 5), although we have not attempted to isolate the compound.

The interesting degree of acrylate cyclization selectivity shown in the diacrylate porphyrin series provides a means of synthesizing a variety of other bacteriochlorin derivatives from unsymmetrical porphyrins with long wavelength absorption and potential application to the field of photodynamic therapy or artificial photosynthesis. We have recently expanded this work to 5,15-diarylporphyrins, the results of which will be reported elsewhere.

Experimental

Silica gel 60 (230–400 mesh) was used for column chromatography. Analytical thin layer chromatography was performed on Merck 60 F254 silica gel (precoated on aluminum). ^1H spectra were recorded using a Unity Inova Varian 500 MHz spectrometer, chemical shifts of proton spectra are expressed in parts per million relative to the chloroform signal in deuterated chloroform (set at 7.24 ppm). Electronic spectra were recorded on a Beckman DU 640 or a Cary 1bio spectrophotometer. High resolution mass spectra were obtained on a VG 70SE double focusing mass spectrometer equipped with an oversize data system at the University of California Santa Barbara by Dr James Povlavek. This method was preferred over elemental analyses as in most cases the compounds retained solvents of crystallization.[8]

Nickel 5,10-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (4) and nickel 5,15-bis[β-(ethoxycarbonyl)vinyl]-octaethylporphyrin (3). Nickel 5-[β-(ethoxycarbonyl)-vinyl]octaethylporphyrin (5.0 g) was dissolved in dichloroethane (200 mL) and 10 g of Vilsmeier reagent was added. The solution was warmed at 65°C for 2 h after which no starting material remained. A saturated sodium acetate solution (100 mL) was added and the solution was heated at 65°C for a further 3 h with rapid stirring. The organic layer was collected and rotoevaporated to dryness. The solid was dissolved in dichloromethane (20 mL) and chromatographed on silica using dichloromethane as solvent. The major green fraction was collected and evaporated to dryness. The next day the solid was dissolved in DMF (70 mL) and carbethoxymethylene triphenylphosphorane (10 g) was added. Argon was bubbled through the solution for 15 min and the solution was then heated at reflux under argon for 8 h, after which no starting material remained. The DMF was removed by rotary evaporation and the solid was dissolved in dichloromethane (70 mL). The solution was chromatographed on silica using 40% hexane/dichloromethane as eluent, and the major red fraction collected. The solvent was removed by rotary evaporation. The red solid was dissolved in toluene (20 mL) and chromatographed on silica using toluene as eluent. Two major

fractions were collected, each being crystallized from dichloromethane/ethanol. The first green fraction eluted was nickel 5,15-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**3**). Yield=3.0 g (54%).

^{1}H NMR: ($CDCl_3$) δ=1.29 (t, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.59 (t, 12H, 4×$CH_2C\mathbf{H}_3$), 1.65 (t, 12H, 4×$CH_2C\mathbf{H}_3$), 3.67 (m, 16H, 8×$C\mathbf{H}_2$), 4.257 (q, 4H, 2×$CO_2C\mathbf{H}_2$), 5.22 (d, 2H, *vinylic*-**H**), 9.17 (s, 2H, *meso*-**H**), 9.87 (d, 2H, *vinylic*-**H**) ppm.

The second green fraction was the nickel 5,10-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin. Yield=3.0 g.

^{1}H NMR: ($CDCl_3$) δ=1.29 (t, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.52 (t, 6H, 2× $CH_2C\mathbf{H}_3$), 1.61 (t, 6H, 2×$CH_2C\mathbf{H}_3$), 1.64 (t, 6H, 2× $CH_2C\mathbf{H}_3$), 1.7 (t, 6H, 2×$CH_2C\mathbf{H}_3$), 3.68 (m, 16H, 8×$C\mathbf{H}_2$), 4.26 (q, 4H, 2×$CO_2C\mathbf{H}_2$), 5.18 (d, 2H, *vinylic*-**H**), 9.16 (s, 2H, *meso*-**H**), 9.87 (d, 2H, *vinylic*-**H**) ppm.

5,10-Bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (5). Nickel 5,10-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (2.0 g) was dissolved in dichloromethane (70 mL) and conc. sulfuric acid (10 mL) was added. The solution was stirred until the dichloromethane layer was colorless and then poured into a saturated bicarbonate solution (100 mL). The reaction flask was rinsed with dichloromethane/water solution and this was added to the reaction flask. The organic layer was collected and reduced in volume to ~25 mL. The organic layer was passed over a pad of silica gel using 2% acetone/dichloromethane as eluent and the major green fraction collected. The solvent was removed by rotary evaporation and the solid residue redissolved in dichloromethane (20 mL). Methanol (30 mL) was added and the dichloromethane removed by rotary evaporation. The precipitated porphyrin was collected by filtration, washed with methanol and pumped to dryness. Yield=1.7 g of 5,10-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**5**). ^{1}H NMR properties were identical to those described in the literature.[4]

5,15-Bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (6). Nickel 5,15-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (1.0 g) was dissolved in dichloromethane (30 mL) and conc. sulfuric acid (7 mL) was added. The solution was stirred until the dichloromethane layer was colorless and then poured into a saturated bicarbonate solution (100 mL). The reaction flash was rinsed with dichloromethane/water solution and this was added to the reaction flask. The organic layer was collected and reduced in volume to ~25 mL. The organic layer was passed over a pad of silica gel using 2% acetone/dichloromethane as eluent and the major green fraction collected. The solvent was removed by rotary evaporation and the solid residue redissolved in dichloromethane (20 mL). Methanol (30 mL) was added and the dichloromethane removed by rotary evaporation. The precipitated porphyrin was collected by filtration, washed with methanol and pumped to dryness. Yield=0.7 g of 5,15-bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**6**). Spectral properties were identical to those described in the literature.[4]

5,15-Octaethylbacteriopurpurin (13b) and 15-[β-(ethoxycarbonyl)vinyl]octaethylpurpurin (14). 5,15-Bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**6**) (60 mg) was dissolved in toluene (20 mL) and DBU (0.1 mL) was added. The solution was refluxed under argon for 5 h after which the solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane (10 mL) and columned on silica using dichloromethane as eluent. The major bright green fraction was collected and rotary evaporated to dryness. The solid was dissolved in dichloromethane (5 mL) and methanol (10 mL) was added. The dichloromethane was removed by slow rotary evaporation and the solid bacteriopurpurin collected by filtration. The solid was pumped dry under vacuum to give 46 mg (76%). ^{1}H NMR shows the compound to be 5,15-octaethylbacteriopurpurin (**13b**).

^{1}H NMR: ($CDCl_3$) δ=−0.16 (t, 6H, $C\mathbf{H}_3$ of sp^3 ethyls), 0.59 (s, 2H, N**H**), 1.54 (t, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.63 (t, 6H, $CH_2C\mathbf{H}_3$), 1.65 (t, 6H, $CH_2C\mathbf{H}_3$), 1.699 (t, 6H, $CH_2C\mathbf{H}_3$), 1.69 (m, 2H, C**H** of sp^3 ethyls), 2.62 (m, 2H, C**H** of sp^3 ethyl's), 2.93 (m, 2H, C**H** of sp^3 ethyls), 3.17 (m, 2H, C**H** of sp^3 ethyl), 3.5–3.9 (m, 10H, 4×$C\mathbf{H}_2$ and 2×C**H**), 4.49 (oq, 4H, 2×$CO_2C\mathbf{H}_2$), 8.40 (brs, 2H, *meso*-**H**), 9.22 (s, 2H, 2×isocyclic ring **H**) ppm. Accurate mass Cal: 730.44578 (exact), Found: 730.44625. UV/vis: λ_{max} nm, ($CHCl_3$/IPA(1:1), ϵ(M^{-1} cm^{-1}); 365 (27,230), 416 (55,000), 556 (11,750), 593 (78,540), 767 (6580), 846 (70,900).

A second polar minor green/brown band was eluted from the column using 2% acetone/dichloromethane. The solvent was removed by rotary evaporation. Yield=5 mg. ^{1}H NMR showed the compound to be 15-[β-(ethoxycarbonyl)-vinyl]octaethylpurpurin (**14**).

^{1}H NMR: ($CDCl_3$) δ=−0.6 (brs, 1H, N**H**), −0.21 (s, 3H, $C\mathbf{H}_3$ of sp^3 methyl), 0.05 (brs, 1H, N**H**), 1.404 (t, 3H, $CO_2CH_2C\mathbf{H}_3$), 1.45 (t, 3H, $CO_2CH_2C\mathbf{H}_3$), 1.54 (t, 3H, $C\mathbf{H}_3$), 1.56 (t, 3H, $C\mathbf{H}_3$), 1.62 (t, 3H, $C\mathbf{H}_3$), 1.64 (m, 2H, C**H** of sp^3 ethyl), 1.65 (t, 3H, $C\mathbf{H}_3$), 1.68 (t, 3H, $C\mathbf{H}_3$), 2.72 (m, 2H, C**H** of sp^3 ethyl), 3.07 (m, 2H, C**H** of sp^3 ethyl), 3.07 (m, 2H, C**H** of sp^3 ethyl), 3.24 (s, 6H, $C\mathbf{H}_3$), 3.41 (s, 3H, $C\mathbf{H}_3$), 3.72 (q, 2H, $C\mathbf{H}_2CH_3$), 3.5–4.0 (om, 13H, 6×$C\mathbf{H}_2$ and C18-**H**), 4.41 (q, 2H, $CO_2C\mathbf{H}_2CH_3$), 4.51 (q, 2H, $CO_2C\mathbf{H}_2CH_3$), 6.12 (d, 1H, *vinylic*-H), 8.61 (s, 1H, *meso*-**H**), 9.28 (s, 1H, isocyclic ring **H**[†]), 9.40 (s, 1H, *meso*-**H**[†]), 9.98 (d, 1H, *vinylic*-H) ppm. Accurate mass calculated 730.44578 (exact), Found: 730.44628.

5,10-Octaethylbacteriopurpurin (17a,b) and 10-[β-(ethoxycarbonyl)vinyl]octaethylpurpurin (16). 5,10-Bis[β-(ethoxycarbonyl)vinyl]octaethylporphyrin (**5**) (200 mg) was dissolved in toluene (30 mL) and DBU (0.1 mL) was added. The solution was refluxed under argon for 24 h after which the solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane (10 mL) and columned on silica using dichloromethane as eluent. Two major fractions were collected and rotary evaporated to dryness. The first bright green fraction corresponded to the desired bacteriopurpurin that could not be induced to crystallize. Yield=100 mg (50%). Proton NMR showed the compound to be a 50:50 mixture of geometric

[†] Assignments may be interchanged as no CH correlation experiments were performed.

cyclization isomers of 5,10-octaethylbacteriopurpurins (**17a,b**).

^{1}H NMR: ($CDCl_3$) δ=−0.29 (s, 1H, N**H**), −0.21 and −0.13* (2×t, 6H, C**H**$_3$ of sp^3 ethyls), 0.03 (s, 1H, N**H**), 1.53 (t, 6H, 2×$CO_2CH_2CH_3$), 1.58–1.72 (ot, 18H, CH_2CH_3), 1.76 (m, 2H, C**H** of sp^3 ethyls), 2.61 (m, 2H, C**H** of sp^3 ethyls), 2.92 (m, 2H, C**H** of sp^3 ethyls), 3.16 (m, 2H, C**H** of sp^3 ethyl), 3.5–3.9 (m, 10H, 4×C**H**$_2$ and 2×C**H**), 4.48 and 4.49 (oq, 4H, CO_2CH_2), 8.41 and 8.44* (2×brs, 2H, *meso*-**H**), 9.195 and 9.197 (2×s, 2H, 2×isocyclic ring **H**) ppm. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 370 (36,960), 434 (56,650), 563 (19,770), 598 (81,090), 796 (13,430), 863 (52,500). Accurate mass calculated 730.44578 (exact), Found: 730.44615. The second green fraction was the 10-[β-(ethoxycarbonyl)vinyl]octaethylpurpurin (**16**) which was crystallized from dichloromethane/methanol, filtered and pumped dry. Yield=90 mg (45%).

^{1}H NMR: ($CDCl_3$) δ=−0.40 (t, 3H, C**H**$_3$ of sp^3 methyl), −0.25 (s, 1H, N**H**), 0.49 (s, 1H, N**H**), 1.33 (t, 6H, 2×$CO_2CH_2CH_3$), 1.48 (t, 3H, C**H**$_3$), 1.53 (t, 3H, C**H**$_3$), 1.60 (t, 3H, C**H**$_3$), 1.61–1.8 (ot,m 13H, 4×C**H**$_3$ and C**H** of sp^3 ethyl), 2.95 (m, 1H, C**H** of sp^3 ethyl), 3.15 (m, 2H, 2×C**H** of sp^3 ethyl), 3.6–3.9 (m, 13H, C**H** and 6×C**H**$_2$), 4.30 (m, 2H, $CO_2CH_2CH_3$), 4.50 (m, 2H, $CO_2CH_2CH_3$), 5.52 (d, 1H, *vinylic*-**H**), 9.24 (s, 1H, *meso*-**H**‡), 9.29 (s, 1H, isocyclic ring **H**‡), 9.39 (s, 1H, *meso*-**H**‡), 9.48 (d, 1H, *vinylic*-**H**) ppm. Accurate mass calculated 730.44578 (exact), Found: 730.44525. UV/vis: λ_{max} nm ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 429 (150,700), 505 (7900), 532 (10,700), 570 (21,400), 643 (8800), 700 (39,700).

Nickel 5,15-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I (10). Nickel 5,15-diformyl etioporphyrin I (**8**) (12.0 g) and carbethoxymethylene triphenylphosphorane (28 g) was dissolved in DMF (100 mL) and argon was bubbled through the solution for 15 min. The solution was heated at reflux under argon for 8 h after which no starting material remained. The DMF was removed by rotary evaporation and the solid dissolved in dichloromethane (200 mL). MeOH (100 mL) was added and the dichloromethane removed by rotary evaporation. The precipitated solid was collected by filtration and dried. The solid was redissolved in hexane/dichloromethane (500 mL) and the solution chromatographed on silica (500 g) using 40% hexane/dichloromethane as eluent, and a minor fraction collected and discarded. The column was then eluted with 25% hexane/dichloromethane and the major green fraction collected and rotoevaporated to dryness. The solid was redissolved in dichloromethane (150 mL) and methanol (150 mL) added. The dichloromethane was removed by rotary evaporation and the precipitated solid collected by filtration and vacuum dried. Yield=9.0 g (85%) of Ni (II) 5,15-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I (**10**).

^{1}H NMR: ($CDCl_3$) δ=1.30 (t, 6H, 2×$CO_2CH_2CH_3$), 1.57 (t, 12H, 4×CH_2CH_3), 1.60 (t, 12H, 4×CH_2CH_3), 3.19 (s, 6H, 2×C**H**$_3$), 3.23 (s, 6H, 2×C**H**$_3$), 3.65 (q, 4H, 2×C**H**$_2$), 3.18 (q, 4H, 2×C**H**$_2$), 4.27 (q, 4H, 2×CO_2CH_2), 5.25 (d, 2H, *vinylic*-**H**), 9.19 (s, 2H, *meso*-**H**), 9.84 (d, 2H, *vinylic*-**H**) ppm. FAB mass calculated 730 (M+), Found: 730 (M+). UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 423 (150,200), 590 (15,300).

Nickel 5,10-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I (9). Nickel 5,10-bis-formyl etioporphyrin I (**7**) (12.0 g) and carbethoxymethylene triphenylphosphorane (28 g) was dissolved in DMF (100 mL) and argon was bubbled through the solution for 15 min. The solution was heated at reflux under argon for 8 h after which no starting material remained. The DMF was removed by rotary evaporation and the solid dissolved in dichloromethane (200 mL). EtOH (100 mL) was added and the dichloromethane removed by rotary evaporation. The precipitated solid was collected by filtration and dried. The solid was redissolved in hexane/dichloromethane (200 mL) and the solution chromatographed on silica (500 g) using 25% hexane/dichloromethane as eluent, and a minor fraction collected and discarded prior to the collection of the main band. The major green fraction was collected and rotoevaporated to dryness. The solid was redissolved in dichloromethane (150 mL) and EtOH (100 mL) added. The dichloromethane was removed by rotary evaporation and the precipitated solid collected by filtration and vacuum dried. Yield=11.5 g of Ni (II) 5,10-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I (**9**).

^{1}H NMR: ($CDCl_3$) δ=1.29 (t, 3H, $CO_2CH_2CH_3$), 1.30 (t, 3H, CH_2CH_3), 1.57 (t, 3H, CH_2CH_3), 1.58 (t, 3H, CH_2CH_3), 1.63 (t, 3H, CH_2CH_3), 3.13 (s, 3H, C**H**$_3$), 3.14 (s, 3H, C**H**$_3$), 3.21 (s, 3H, C**H**$_3$), 3.24 (s, 3H, C**H**$_3$), 3.58–3.72 (m, 8H, 4×C**H**$_2$), 4.255 (q, 2H, CO_2CH_2), 4.27 (q, 2H, CO_2CH_2), 5.21 (d, 1H, *vinylic*-**H**), 5.24 (d, 1H, *vinylic*-**H**), 9.15 (s, 1H, meso-**H**), 9.16 (s, 1H, meso-**H**), 9.77 (d, 1H, *vinylic*-**H**), 9.83 (d, 1H, *vinylic*-**H**) ppm. Accurate mass calculated 730.3029, Found: 730.3030. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 425 (74,900), 580 (9215).

5,10-Bis[β-(ethoxycarbonyl)vinyl]etioporphyrin (11). Nickel 5,10-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I (**9**) (1.0 g) was dissolved in dichloromethane (50 mL) and concentrated sulfuric acid (10 mL) was added. The solution was stirred until the dichloromethane layer was colorless and then poured into a saturated sodium bicarbonate solution (100 mL). The reaction flask was rinsed with dichloromethane/water and this was added into the bicarbonate solution. Methanol (30 mL) was added and the dichloromethane was removed by rotary evaporation. The precipitated porphyrin was collected by filtration, washed with methanol and pumped to dryness. Yield=0.85 g of 5,10-bis-acrylate etioporphyrin (**11**). The organic layer was collected and reduced in volume to ~20 mL. The organic solution was passed over a column of silica using 2% acetone dichloromethane as eluent and the major green fraction collected. The solvent was removed by rotary evaporation and the solid redissolved in dichloromethane (20 mL). Methanol (30 mL) was added and the dichloromethane was removed by rotary evaporation. The precipitated porphyrin was collected by filtration, washed with methanol and pumped to dryness. Yield=0.85 g of 5,10-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin (**11**).

‡ No CH correlation experiments were performed to definitively assign peaks.

^{1}H NMR: ($CDCl_3$) δ=−2.38 (brs, 2H, N**H**), 1.37 (t, 3H, $CH_2C\mathbf{H}_3$), 1.47(t, 3H, $CO_2CH_2C\mathbf{H}_3$), 1.48 (t, 3H, $CO_2CH_2C\mathbf{H}_3$), 1.69 (t, 3H, C$\mathbf{H}_3$), 1.72 (t, 3H, C$\mathbf{H}_3$), 1.77 (t, 3H, C$\mathbf{H}_3$), 2.88(s, 3H, C$\mathbf{H}_3$), 3.31 (q, 2H, C$\mathbf{H}_2$), 3.39 (s, 6H, 2×C$\mathbf{H}_3$), 3.45 (s, 3H, C$\mathbf{H}_3$), 3.89 (m, 6H, 3×C$\mathbf{H}_2$), 4.47 (q, 4H, 2×$CO_2C\mathbf{H}_2$), 6.24 (d, 1H, *vinylic***H**), 6.35 (d, 1H, *vinylic*-**H**), 9.61 (s, 1H, *meso*-**H**), 9.62 (s, 1H, *meso*-**H**), 10.15 (d, 2H, *vinylic*-**H**), 10.20 (d, 2H, *vinylic*-**H**) ppm. Accurate mass calculated 675.391 (M $+H^+$), Found: 675.3907. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 430 (73,500), 522 (8,300), 592 (6,400).

5,15-Bis[β-(ethoxycarbonyl)vinyl]etioporphyrin (12). Nickel 5,15-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin I (**10**) (0.2 g) was dissolved in dichloromethane (50 mL) and concentrated sulfuric acid (5 mL) was added. The solution was stirred until the dichloromethane layer was colorless, then ice water (150 mL) was added. A solution of saturated sodium bicarbonate (50 mL) was added carefully to the solution and the organic layer separated and washed with water (100 mL). The organic layer was collected and dried over sodium sulfate, filtered and evaporated to dryness. The solid was dissolved in dichloromethane (20 mL) and methanol (10 mL) added. The dichloromethane was removed by rotary evaporation and the precipitated pink flocculate collected by filtration, washed with ethanol and pumped to dryness. Yield= 170 mg of 5,15-bis[β-(ethoxycarbonyl)vinyl]etioporphyrin (**12**).

^{1}H NMR: ($CDCl_3$) δ=−2.38 (brs, 1H, N**H**), 1.44 (t, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.62 (t, 6H, 2×$CH_2C\mathbf{H}_3$), 1.76 (t, 6H, 2×$CH_2C\mathbf{H}_3$), 3.32 (s, 6H, 2×CH_3), 3.56 (s, 6H, 2×CH_3), 3.87 (q, 4H, 2×C$\mathbf{H}_2$), 3.97 (q, 4H, 2×C$\mathbf{H}_2$), 4.45 (q, 4H, 2×$CO_2C\mathbf{H}_2$), 6.20 (d, 2H, *vinylic*-**H**), 10.05 (s, 2H, *meso*-**H**), 10.18 (d, 2H, *vinylic*-H) ppm. Accurate mass calculated 674.3832, Found: 674.3838. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 414 (156,140), 511(9,830) 548 (5,540), 579 (6,630), 634 (2,860).

5,15-Ethyletiobacteriopurpurin (20). 5,15-Bis[β-(ethoxycarbonyl)vinyl]etioporphyrin (**12**) (200 mg) was dissolved in toluene (20 mL) and DBU (0.1 mL) was added. The solution was refluxed under argon for 5 h after which the solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane (10 mL) and columned on silica using dichloromethane as eluent. The major bright green fraction was collected and rotary evaporated to dryness. The solid was dissolved in dichloromethane (5 mL) and methanol (10 mL) was added. The dichloromethane was removed by slow rotary evaporation and the solid bacteriopurpurin collected by filtration. The solid was pumped dry under vacuum to give 175 mg (88%) of a compound shown by ^{1}H NMR to be 5,15-ethyletiobacteriopurpurin (**20**).

^{1}H NMR: ($CDCl_3$) δ=−0.079 (t, 6H, C$\mathbf{H}_3$ of sp^3 ethyls), 0.61 (s, 2H, N**H**), 1.54 (t, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.57 (t, 6H, $CH_2C\mathbf{H}_3$), 1.65 (m, 2H, 2×C**H** of sp^3 ethyls), 2.35 (d, 3H, C$\mathbf{H}_3$), 2.57 (m, 2H, 2×C**H** of sp^3 ethyls), 3.33 (s, 3H, ring C$\mathbf{H}_3$), 3.58 (m, 4H, 2×C$\mathbf{H}_2$), 4.20 (q, 2H, **CH**), 4.49 (q, 4H, 2×$CO_2C\mathbf{H}_2$), 8.19 (s, 2H, *meso*-**H**), 9.29 (s, 2H, 2×isocyclic ring **H**) ppm. Accurate mass Cal: 674.3832 (exact), Found: 674.3817. UV/vis: λ_{max} nm, ($CHCl_3$/IPA(1:1), ϵ(M^{-1} cm^{-1}); 364 (32,100), 415 (60,600), 439 (40,600), 558 (15,800), 592 (79,300), 768 (8,300), 843 (70,800).

5,15-Methyletiobacteriopurpurin (21). The methanol mother liquors from the preceding step were evaporated to dryness and redissolved in dichloromethane (1 mL). Hexane (2 mL) was added and the dichloromethane removed warming over a water bath. The solution was left overnight and resulting crystals filtered and dried under vacuum. Yield=10 mg.

^{1}H NMR: ($CDCl_3$) δ=0.45 (s, 2H, N**H**), 1.26(s, 6H, C$\mathbf{H}_3$ of sp^3 ethyls), 1.53 (t, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.66 (t, 6H, $CH_2C\mathbf{H}_3$), 1.71 (t, 6H, $CH_2C\mathbf{H}_3$), 2.91 (m, 2H, 2×C**H** of sp^3 ethyls), 3.17(s, 6H, ring C$\mathbf{H}_3$), 3.18 (m, 2H, 2×C**H** of sp^3 ethyls), 3.75 (m, 6H, 2×C$\mathbf{H}_2$, 2×C**H**), 4.50 (q, 4H, 2×$CO_2C\mathbf{H}_2$), 8.45 (s, 2H, *meso*-**H**), 9.16 (s, 2H, 2×isocyclic ring **H**) ppm. Accurate mass calculated 674.3832 (exact), Found: 674.3821. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 360 (27,570), 412 (51,990), 554 (13,060), 591 (76,360), 761 (7,800), 839 (70,700).

5,10-Etiobacteriopurpurin (27a,b) and 10-[β-(ethoxycarbonyl)vinyl]etiopurpurin (24). 5,10-Bis[β-(ethoxycarbonyl)vinyl]etioporphyrin (**11**) (200 mg) was dissolved in toluene (20 mL) and DBU (0.1 mL) was added. The solution was refluxed under argon for 24 h after which the solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane (10 mL) and columned on silica using dichloromethane as eluent. Two fractions were collected, the first being a bright green fraction, 5,10-etiobacteriopurpurin and the major fraction being 10-[β-(ethoxycarbonyl)vinyl]etiopurpurin (**24**). The two fractions were separately rotoevaporated to dryness. The bacteriopurpurin fraction could not be induced to crystallize. Yield=25 mg (12%). The major purpurin product was dissolved in dichloromethane (10 mL) and methanol (10 mL) was added. The dichloromethane was removed by slow rotary evaporation and the precipitated purpurin collected by filtration. The solid was pumped dry under vacuum to give 155 mg (76%).

5,10-Etiobacteriopurpurin (27a,b). ^{1}H NMR (isomer mixture 50:50): ($CDCl_3$) δ=−0.285 (brs,1H, N**H**), −0.12, −0.069 (2×t, 3H, C$\mathbf{H}_3$ of sp^3 ethyl), 0.03(s, 1H, N**H**), 1.32 (s, 3H, sp^3 C$\mathbf{H}_3$), 1.53 (ot, 6H, 2×$CO_2CH_2C\mathbf{H}_3$), 1.57–1.75 (ot, 9H, $CH_2C\mathbf{H}_3$), 2.35 (2×d, 3H, C$\mathbf{H}_3$), 2.55 (m, 1H, C**H** of sp^3 ethyls), 2.70 (m, 1H, 2×C**H** of sp^3 ethyls), 3.14 (brs, 3H, ring C$\mathbf{H}_3$), 3.36, 3,34 (brs, 3H, ring C$\mathbf{H}_3$), 3.5–3.9 (om, 4.5H, 0.5×H, 2×C$\mathbf{H}_2$), 4.06 (br q, 1/2H, C**H**), 4.48, 4.49 (oq, 4H, 2×$CO_2C\mathbf{H}_2$), 8.24, 8.27 (s, 1H, *meso*-**H**), 8.44, 8.47 (s, 1H, *meso*-**H**), 9.12, (s, 1H, isocyclic ring **H**), 9.26 (s, 1H, isocyclic ring **H**), ppm. Accurate mass calculated 674.3832 (exact), Found: 674.3821. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}, 369 (36,680), 434 (56,220), 561 (19,620), 597 (80,500), 795 (13,330), 862 (52,100).

10-[β-(Ethoxycarbonyl)vinyl]etiopurpurin (24). ^{1}H NMR: ($CDCl_3$) δ=−0.381 (brs, 1H, N**H**), −0.32 (t, 3H, C$\mathbf{H}_3$ of sp^3 ethyl), 0.33 (brs, 1H, N**H**), 1.35 (t, 3H, $CO_2CH_2C\mathbf{H}_3$), 1.50 (m, 1H, CH of sp3 ethyl), 1.52 (t, 3H, C$\mathbf{H}_3$), 1.54 (t, 3H,

C**H**$_3$), 1.65 (t, 3H, C**H**$_3$), 1.67 (t, 3H, C**H**$_3$), 2.50 (d, 3H, CH_3), 2.58 (m, 1H, C**H** of sp^3 ethyl), 3.23 (s, 6H, C**H**$_3$), 3.35 (s, 3H, C**H**$_3$), 3.45 (s, 3H, C**H**$_3$), 3.6–3.9 (om, 6H, 3×C**H**$_2$), 4.33 (q, 2H, CO_2**C**H_2CH_3), 4.495 (q, 2H, CO_2C**H**$_2CH_3$), 4.58 (q, 1H, C18-**H**), 5.59 (d, 1H, *vinylic*-H), 9.27 (s, 1H, *meso*-**H**), 9.42 (s, 2H, isocyclic ring H and *meso*-**H**), 9.53 (d, 1H, *vinylic*-**H**) ppm. UV/vis: λ_{max} nm, ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 430 (150,800), 503 (7,850), 531(10,650), 570 (21,340), 643 (8,710), 701 (39,600). Accurate mass calculated 674.3832 (exact), Found: 674.3831.

5,15-Bacterioetiochlorin (28). 5,15-Etiobacteriopurpurin (**20**) (50 mg) was dissolved in tetrahydrofuran (15 mL) and Pd/C (200 mg) added. The solution was hydrogenated under a hydrogen atmosphere for 24 h. An aliquot of the solution, re-oxidized with air showed the absence of any starting material (844 nm) or of mono reduction (806 nm). The solution was filtered to remove the Pd/C catalyst and the solution stirred for 0.5 h in the presence of air. The solution was evaporated to dryness and the crude residue was dissolved in dichloromethane and methanol was added. The dichloromethane was removed by rotary evaporation and the precipitated bacteriochlorin was collected by filtration, washed with methanol, and dried. Yield=40 mg.

^{1}H NMR: ($CDCl_3$) δ=−0.75 (brs, 2H, N**H**), −0.15 (t, 6H, C**H**$_3$ of sp^3 ethyl), 1.4–1.65 (ot, 15H 3×CH_3, 2×CO_2CH_2C**H**$_3$), 1.75 (m, 4H, CH of sp3 ethyl), 2.15 (d, 6H, 2×C**H**$_3$), 2.58 (m, 1H, C**H** of sp^3 ethyl), 3.22 (s, 6H, C**H**$_3$), 3.65 (om, 6H, 3×C**H**$_2$), 4.09 (m, 2H, 2×isocyclic ring H), 4.45 (om, 6H, 2×CO_2C**H**$_2CH_3$, 2×C**H**), 4.62 (dofd, 2H, 2×isocyclic ring **H**), 4.92 (m, 2H, 2×isocyclic ring **H**), 8.07 (s, 2H, *meso*-**H**) ppm.

λ_{max} nm ($CHCl_3$/IPA (1:1), ϵ(M^{-1} cm^{-1}); 761 (89,730), 725 (11,238), 696 (9,372), 517 (37,190), 487 (13,320), 454 (13,320), 385 (100,100), 357 (85,300). Accurate mass calculated 676.3988 (exact), Found: 676.3981.

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