Published in final edited form as:

J Org Chem. 2009 January 16; 74(2): 568–579. doi:10.1021/jo8019237.

Remarkable Features of the McMurry Reaction Conditions in Dimerization of Formyl- and 2-Formylvinylpurpurinimides. Electrochemistry of Monomeric Ni(II) Purpurinimide and the Corresponding Dyads

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Abstract

To investigate the electrochemical properties of purpurinimide dyads and electron transfer sites for their reduction and oxidation, a series of dimers with variable C-C linkages were synthesized. For the preparation of these novel structures, the formyl and 2-formylvinyl substituents were regioselectively introduced at positions-3 and 20 of Ni(II) purpurinimides by the Vilsmeier reaction. The Ni(II) complexes were then subjected to the McMurry reaction under two different conditions with unexpected results being obtained. For example, the reaction of formyl purpurinimides with $\text{TiCl}_3(\text{DME})_{1.5}$ failed to produce the desired C-C dimers and the starting compounds were recovered almost quantitatively. Under similar reaction conditions, the 20-(2-formylvinyl)purpurinimide also did not dimerize but gave instead unexpected benzoisobacteriochlorins *via* an intramolecular cyclization. However, treatment of the 3-formyl- and 20-formyl-purpurinimides with TiCl_4/Zn gave the corresponding dimers linked with one double bond (*trans*-) in modest yields. Under similar conditions, Ni(II) purpurinimides containing a 2-formylvinyl substituent either at position-3 or position-20 afforded the respective C-C dimers, where the purpurinimide moieties were joined with a *trans-trans-trans*- hexatriene linker. Molecular modeling data suggest that the nature of the conformational energy difference found in all *trans*- vs. *trans-cis-trans*- conformers of the dimers connected by a hexatriene linker at the *meso*- or β -position of the macrocycle is not due to the intrinsic conformational energy difference of the linker region, which is identical for both dimers.

Introduction

The McMurry reaction dealing with the use of low-valent titanium complexes has been extensively used for reductive coupling of carbonyls to olefins.¹ It is an exceptionally versatile bond construction method in organic synthesis and in many cases, the best approach for the preparation of highly complex and strained cyclic ring systems.² This reaction is usually carried out in two steps: reduction of TiCl_4 or TiCl_3 , followed by addition of the carbonyl substrate.

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Supporting Information Available: NMR spectra of compounds 4–6, 10–13, 15–19, UV-vis spectra of compounds 13, 15, 18 and 19. This material is available free of charge via the Internet at <http://pubs.acs.org>

The nature of the titanium reagent, as well as the solvent, temperature and reaction time, have a strong influence on eventual formation of the resulting product. Several improved procedures are known in the literature for the preparation of homo dimers and the recommended 'optimized method' is to use a $\text{TiCl}_3(\text{DME})_{1.5}\text{-Zn}(\text{Cu})$ combination.³

We were interested in extending this approach to the purpurinimide system for a number of reasons. In our previous studies with a series of porphyrin and chlorin-fullerene systems we have shown that the presence of a purpurinimide moiety makes a significant impact in producing long lived charge-separated states,^{4–6} and such a characteristic could be useful in designing improved synthetic models to understand the initial charge separation process in photosynthesis. The purpurinimide system also provides an enormous opportunity to introduce carbonyl substituents at the peripheral (3, 8 and 12, N-substitution) and *meso*-positions of the macrocycle, which could help to generate supramolecular structures with fixed distances and orientation.^{7–11} This would allow a comparison between the electrochemistry of monomeric Ni(II) chlorins and the corresponding dyads linked by one or three double bonds at the *meso*- or peripheral positions to give fixed orientations. Finally, we have previously shown that certain biologically inactive porphyrin monomers showed enhanced *in vivo* efficacy when converted into the corresponding dimers with carbon-carbon linkages between the two macrocycles.^{12,13} Thus, there was a good possibility that single purpurinimides having a long wavelength absorption (700 nm) and high singlet oxygen producing efficiency (>50%) might show improved PDT efficacy upon conversion to the corresponding dimers (nonmetallated analogs). Finally, it was thought that under controlled conditions, the McMurry approach might be useful in developing heterodimers joined with C-C linkages.

The utility of the McMurry reaction in porphyrin chemistry has been explored in depth by Vicente and Smith¹⁴ who showed that metalloformylporphyrins, metallo(2-formylvinyl) porphyrins and chlorins upon reacting with $\text{TiCl}_3(\text{DME})_{1.5}\text{-Zn}(\text{Cu})$ could be efficiently dimerized, giving bis-macrocyclic compounds which were linked with either one or three carbon-carbon double bonds. This approach was further extended to the pyropheophorbide system, to obtain planar bis-chlorin derivatives with a completely conjugated π system.¹⁵ This coupling approach has also been used by Vogel and co-workers in the preparation of the porphycene class of pyrrole macrocycles.¹⁶ Interestingly, in our hands the reaction of purpurinimide analogs containing a formyl- or 2-formylvinyl substituent with $\text{TiCl}_3(\text{DME})_{1.5}\text{-Zn}(\text{Cu})$ did not produce the desired dimers. Instead, the formyl derivatives were found to be inactive, whereas the 2-formylvinyl analogs produced benzoisobacteriopurpurinimides as the main products *via* intramolecular cyclization. However, following the modified McMurry reaction conditions ($\text{TiCl}_4\text{-Zn}$) reported by Mukaiyama et al.¹⁷ afforded the dimeric species in modest yields.

Results and Discussion

For preparation of dimers with variable carbon linkages joined either at the *meso*- or peripheral positions, purpurin-18-N-hexylimide **1** was used as a substrate, which in turn was obtained from methyl pheophorbide-*a* by following the literature procedure.¹⁸ Reaction of **1** with Ni(acac)₂ and a subsequent treatment with Pd/C under a hydrogen atmosphere afforded the Ni(II) mesopurpurin-18-N-hexylimide **3** in almost quantitative yield, which, upon further treatment with POCl_3/DMF under Vilsmeier reaction conditions, gave the 20-*meso*-formyl analog **4** in excellent yield. Under similar reaction conditions, the reaction of **3** with 3-(dimethylamino) acrolein and phosphoryl chloride (3-DMA/ POCl_3) gave the corresponding 20-formylvinyl purpurinimide **5** in 75% yield. The 20-formyl purpurinimide **4** upon being subjected to the reductive coupling reaction under conditions reported by Vicente and Smith¹⁴ [the active titanium reagent was prepared by refluxing a slurry containing 9.9 equiv of $\text{TiCl}_3(\text{DME})_{1.5}$ and 35.5 equiv of Zn-Cu couple for 2h in 1,2-dimethoxyethane(DME)] did

not form the expected dimers. Instead, the starting meso-formyl compound **4** was isolated almost quantitatively, whereas the formylvinyl analog produced the isobacteriopurpurinimide **6** as a sole product. Subjecting the purpurinimide **10**, in which the N-hexyl group was replaced with 3,5-bis(trifluoromethyl) benzyl group using a similar McMurry reaction condition, afforded the cyclic products **11** (major) and **12** (minor) in which the acrolein group cyclized onto the adjacent pyrrole subunit (see Scheme 2). Leaving the reaction for a longer time produced mainly the isobenzochlorin analog **11**. The structures of both cyclic products were confirmed by comparative ^1H NMR studies (Figure 1).

The formation of such a cyclic structure from the *meso*-(2-formylvinyl) substituted porphyrins via acid catalyzed conditions have previously been reported by us^{19–22} and others.^{23–28} However, this is the first example showing the utility of the McMurry reaction for the preparation of novel new benzoisobacteriochlorin system.

For the preparation of the desired purpurinimide dyads (homo-dimers), the 3-formyl- and 2-formylvinyl purpurinimides were individually subjected to various modified McMurry reaction conditions and interestingly, upon treating the 20-formylmeso-purpurinimide **4** with TiCl_4/Zn the desired dimer with one carbon-carbon bond **13** was obtained in 42% yield. In the NMR spectrum, the alkene protons appear as a singlet at 7.09 ppm indicating that they are magnetically equivalent and that the dimer molecule has an element of symmetry. Under similar conditions, the reaction of 20-formylvinyl purpurinimide **5** afforded dimer **15** containing a hexatriene linker as a major product. The 2-formyl vinyl group ($-\text{CH}=\text{CH}-\text{CHO}$) in compound **5** consists of a *trans*-confirmation. Therefore, the resulting dimer **15** [Scheme 3] with a triene linkage could exist in either EEE or EZE isomer forms. The NMR analyses of **15** clearly indicates its symmetrical nature and the coupling constant values of the triene protons were found to be 15.0, 6.8 and 2.8 Hz, which corresponds to the J_{ab} , J_{bc} and J_{ac} values of the triene (since the molecule is symmetrical, these values are also equal to $J_{a'b'}$, $J_{b'c'}$ and $J_{a'c'}$, which reflects to a structure having *trans*-, *trans*- and *trans* geometry and agrees with the similar triene system reported in the literature.^{14,29}

The molecular modeling study also indicated that an all *trans*-configuration is more stable than a *trans-cis-trans* configuration from the selected conformations examined for the dimer connected at the *meso*- position. Since there are many rotational degrees of freedom for the 6 carbon linker region, it was not possible to examine all possible conformations. In general, the semi-empirical MO used in this study tends to underestimate the conformational energy differences, but nevertheless, the all *trans*-configuration is about 4 kcal/mol more stable than the *trans-cis-trans* configuration. The energy optimized structures of a possible conformer for all *trans*- and *trans-cis-trans* configurations of the hexatriene in dimer **14** and **15** respectively are shown in Figure 2.

For the preparation of β - β' -linked purpurinimides with one and three double bond carbon units, Ni(II) 3-formylpurpurin-18-N-hexylimide **16** and 3-(2'-formylvinyl-purpurin-18-N-hexylimide **17** were used as substrates and were obtained by reacting Ni(II) purpurinimide **2** with osmium tetroxide/sodium periodate³⁰ and POCl_3/DMF respectively. Reaction of the formyl analogs with TiCl_4/Zn in THF for 30–45 min produced the dimers **18** and **19** in excellent yields. Compared to the dimers connected at the meso positions, slightly different trends were observed by the molecular modeling study for dimers connected at a β -pyrrole position. Again, all possible conformations were not examined, but those selected conformations examined for dimers **19**, **19a** are shown in Figure 3. Among the 7 conformers examined (3 all *trans* configurations, and 4 *trans-cis-trans* configurations), the maximum energy difference was only 2 kcal/mol indicating very similar stabilities among the different conformers. Although the most stable conformer belongs to the all *trans*- configuration, other conformers in all *trans* configurations were very similar in stability to conformers belonging to the *trans-cis-trans*-

configuration. Thus, from the molecular modeling study alone, it is not possible to decide the conformation of the linker regions in dimers formed through linking at the β -position. It is speculated that dimer formation through the meso-position will create a tighter steric hindrance than for the corresponding dimer linked through the β -positions. This in turn restricts the number of possible conformers. From the very similar energies for various conformers in dimers connected through the β -position, it is concluded that the nature of conformational energy difference found in all *trans*- vs. *trans-cis-trans*- conformers for both the dimers connected at the *meso*- or at β -position is not due to the intrinsic conformational energy difference of the linker region, which is identical for both dimers.

Redox Processes

The electrochemistry of Ni(II) purpurinimide **3** and the corresponding dyads **13**, **15**, **18** and **19** was investigated in benzonitrile (PhCN) containing 0.1 M TBAP as supporting electrolyte. Half-wave potentials for each process of the five compounds are given in Table 1 and cyclic voltammograms (CV) of each in PhCN, 0.1 M TBAP are shown in Figure 4.

The monomeric nickel chlorin **3** (top CV in Figure 4) undergoes two reversible one-electron reductions at $E_{1/2} = -0.99$ and -1.43 V and two reversible one-electron oxidations at $E_{1/2} = 0.81$ and 1.11 V. A global addition or abstraction of two electrons also occurs for each macrocycle of the four electrochemically characterized dyads, with the potentials of each process varying with both the position and type of linkage. This is seen from the data in Table 1 where the two dyads with short linkers at the meso (**13**) or β -pyrrole position (**18**) of the macrocycle are both harder to oxidize than the monomeric chlorin **3** by 30~60 mV and easier to reduce by 140~150 mV. Compounds **13** and **18** also exhibit separate half-wave potentials for the first electron addition to each macrocycle, one process occurring at -0.84 to -0.85 V and the other at -0.94 to -0.95 V (see Table 1). Dyads **13** and **18** have a similar HOMO-LUMO gap of 1.69 to 1.71 V as compared to 1.80 V for the monomeric chlorin **3**.

In contrast to the above dyads with short linkers, those with long meso (**15**) or β -pyrrole (**19**) linking groups, are both easier to reduce and easier to oxidize than the monomer **3**. The difference in potential is 70~100 mV on reduction and 50~110 mV on oxidation which leads to a smaller HOMO-LUMO gap of 1.62 to 1.65 V for dyads with the long linkers, as compared to 1.65~1.71 V for dyads **13** and **18** with the short linkers and 1.80 V for the monomeric chlorin **3**. The two macrocycles of dyads **15** and **19** are reduced at the same half-wave potential, indicating a lack of interaction between the two conjugated π systems but this is not the case for oxidation where the two equivalent macrocycles show separate processes for the first electron abstraction, these reactions occurring at $E_{1/2} = 0.70$ or 0.76 V and 0.83 or 0.88 V as seen in Table 1 and Figure 4.

An interaction between the two doubly reduced macrocycles of **18** and **19** is also seen in the cyclic voltammograms of Figure 4. This is most clearly illustrated in the CV of **18** where the reversible addition of a second electron to the two linked macrocycles of the dyad occurs at -1.30 and -1.48 V, as compared to $E_{1/2} = -1.43$ V in the case of compound **3**. The currents for the “split” second reduction of **18** at -1.30 and -1.48 V are about half that of the compound’s single oxidation at 0.87 V and this is consistent with the global addition and abstraction of one electron per macrocycle in each case.

Spectroelectrochemical data indicates that the first electron addition and first abstraction of the five electrochemically characterized dyads involves the conjugated macrocycle and no metal-centered reactions are observed. This is discussed on the following pages.

UV-visible Spectra of Neutral, Electrooxidized and Electroreduced Compounds

Three types of UV-visible spectra were obtained for the investigated compounds. One is for the monomeric chlorin **3** and the other two are for the dyads with meso or β -pyrrole linkers, either long or short as seen in Table 2. The monomeric compound **3** has a split Soret band at 421 and 393 nm, an intense visible band at 664 nm and two additional bands at 544 and 615 nm. All four dyads have a split Soret band and the main difference between spectra of these compounds is in the visible region where the meso-linked **13** and **15** are characterized by two bands at 581 and 695~700 nm and β -pyrrole linked **18** and **19** are characterized by three bands between 556 and 716 nm as seen in Table 2. No major difference in the position of the bands for the neutral compounds is seen upon changing the length of the linker, *i.e.* between **13** (short) and **15** (long) or between **18** (short) and **19** (long) and this is also the case after the global addition or abstraction of one electron per macrocycle in a thin-layer spectroelectrochemical cell.

In order to investigate the site of electron transfer and/or degree of interaction between the two macrocycles in their oxidized and reduced forms, UV-visible spectra of each compound were obtained in a thin-layer cell after oxidation and reduction at a controlled potential and examples of the spectral changes are shown in Figures 5–7 for the monomeric chlorin **3** and the two sets of dyads with long or short linkers at the meso or β -pyrrole position of the macrocycle.

Applying a reducing potential of -1.25 V to a solution of compound **3** in PhCN containing 0.2 M TBAP, leads to a decrease in the initial Soret band in intensity as a new species is formed which has a split Soret band at 380 and 429 nm (Figure 5a). The initial visible band at 664 nm decreases only slightly in intensity upon reduction and is red-shifted to 668 nm but two new visible bands of the reduced product appear at 615 and 760 nm, suggesting formation of a π -anion radical during the first one electron reduction. A split Soret band is also seen after oxidation of **3** at 1.00 V, and under these conditions, major changes occur in the visible region of the spectrum. The spectra of the oxidized species are shown by the dashed red line in Figure 5b. The intense visible band of the neutral compound at 664 nm is no longer present and is replaced by a broad low intensity absorption between 700–800 nm. This type of spectrum suggests of a π -cation radical for the singly oxidized chlorin.

The global addition or abstraction of one electron to each macrocycle of the dyads **13**, **15**, **18** and **19** also gives UV-visible spectra characteristic of π -anion radicals (reduction) and π -cation radicals (oxidation). The final spectra of the electroreduced and electrooxidized products are shown in red in Figures 6 and 7 where comparisons of the dyads can be made as either a function of the length of the linker, short (two left spectra) or long (two right spectra) or as a function of the linker position (meso-linked dyads shown at top of figures and β -linked dyads on bottom).

As indicated above, the major difference in UV-visible spectra of the neutral dyads depends upon the position of the linkage and not the length of the linkers (see black spectra of neutral compounds in Figures 6 and 7) and the same can be said after the addition or abstraction of one electron where the product of the electron transfer reaction is drawn in red in the two figures.

The two singly reduced dyads with meso-linkages have five bands between 350 and 850 nm while those with β -pyrrole linkages have six bands over the same spectral region. Like the spectrum of the singly reduced compound **3**, there is a split Soret band but, unlike compound **3**, the initial Q band is significantly decreased in intensity, suggesting a π -anion radical in each case. The different spectra for the monomeric **3** and the four dyads after reduction may be related to interactions which occur between the two anion radicals in each dyad as is evident from the cyclic voltammograms in Figure 4.

Fewer difference are seen in UV-visible spectra of the electrooxidized dyads, and unlike the case of reductions, the final spectra (Figure 7, red line) closely resemble the spectrum of the singly oxidized compound **3** under the same solution conditions (Figure 5b, red line). In each case, the singly oxidized dyads have a split Soret band and the spectra are similar to that of π -cation radical where one electron is abstracted from each macrocycle of the dyad.

Conclusion

The McMurry reaction provides a unique opportunity to prepare porphyrin-based dimers with fixed orientations. The nature of the titanium reagent shows a strong influence on the eventual formation of the cyclic or dimeric structures and stereochemistry. Poor quality reagents or solvents or the introduction of air result in poor yields of the desired products. An involvement of pinacolate intermediates in the McMurry reaction for the formation of purpurinimide dimers seems to occur as noted in other systems. Each investigated dyad shows behavior similar to the monomeric unit, but changes in the length or position of the linker can result in changes in the electrochemical and spectroelectrochemical properties of the compounds and/or the extent of interaction between the neutral, electroreduced or electrooxidized species. There is no significant difference in UV-visible spectra between the meso and β -linked dyads as a function of the spacer length but the length of the spacer does affect the ease of oxidation and reduction, the resulting HOMO-LUMO gap and the interaction between the two oxidized or reduced units.

Experimental Section

All reactions were carried out in flame-dried glassware under an atmosphere of nitrogen with magnetic stirring. Thin-layer chromatography (TLC) was done on ANALTECH precoated silica gel GF PE sheets (Cat. 159017, layer thickness 0.25 mm) and aluminum oxide NF PE sheets (Cat. 101016, layer thickness 0.2 mm). Column chromatography was performed either over Silica Gel 60 (70–230 mesh) or neutral Alumina (Brockmann grade III, 50 mesh). In some cases preparative TLC plates were also used for the purification (ANALTECH precoated silica gel GF glass plate, Cat. 02013, layer thickness 1.0 mm). Solvents were purified as follows: trace amounts of water and oxygen from THF were removed by refluxing over sodium under an inert atmosphere. Dichloromethane was dried over P_2O_5 . Anhydrous DMF, triethylamine, pyridine and other common chromatographic solvents were obtained from commercial suppliers (J.T. Baker[®], EMD[®] and Aldrich[®]) and used without further purification. NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer. All chemical shifts are reported in parts per million (δ). 1H NMR (400 MHz) spectra were recorded at room temperature in $CDCl_3$ or CD_3OD solutions and referenced to residual $CHCl_3$ (7.26 ppm) or TMS (0.00 ppm). 1H NMR data of the symmetrical dimers are given as their monomer half. EI-Mass spectra were carried out on a Bruker Esquire ion-trap mass spectrometer equipped with a pneumatically assisted electrospray ionization source, operating in positive mode. The high-resolution mass spectrometry analyses were performed at the Mass Spectrometry Facility, Michigan State University. UV-visible spectra were recorded on a Varian Cary 50 Bio UV-visible spectrophotometer using dichloromethane as solvent. All photophysical experiments were carried out using spectroscopic grade solvents.

Ni(II) Purpurin-18-N-hexylimide methyl ester **2**

Purpurin-18-N-hexylimide **1** (610.0 mg, 0.92 mmol) was dissolved in 100 ml of toluene and nickel acetylacetonate hydrate (2.36 mg, 9.2 mmol) was added to it. The reaction mixture was refluxed vigorously for 2 hr and progress of the reaction was monitored by TLC and UV-visible spectroscopy. After completion, the reaction mixture was cooled and filtered through an celite bed, the filtrates concentrated and then directly loaded on a silica column. Product **2** was eluted with 1% acetone/dichloromethane. Yield: 600.0 mg (90.6%). UV-vis λ_{max} (in CH_2Cl_2): 673 nm (ϵ 4.1×10^4), 548 nm (ϵ 0.5×10^4), 423 nm (ϵ 6.9×10^4), 379 nm (ϵ 3.9×10^4). 1H NMR

(400 MHz, CDCl₃): δ 9.02 (s, 1H, meso-H), 8.77 (s, 1H, meso-H), 7.93 (s, 1H, meso-H), 7.58 (dd, 1H, 3-CH=CH₂, J = 11.6 & 17.6 Hz), 5.92 (dd, 2H, 3-CH=CH₂, J = 9.6 & 15.6 Hz), 4.79 (dd, 1H, 17-H, J = 3.2 & 8.8 Hz), 4.28 (m, 2H, N-CH₂-hexyl), 4.07 (q, 1H, 18-H, J = 6.8 Hz), 3.61 (s, 3H, CO₂Me), 3.50 (s, 3H, ring-CH₃), 3.46–3.38 (m, 2H, 8-CH₂CH₃), 3.00 (s, 3H, ring-CH₃), 2.95 (s, 3H, ring-CH₃), 2.65–2.61 (m, 1H, 17²-CHH), 2.59–2.55 (m, 1H, 17²-CHH), 2.22–2.20 (m, 1H, 17¹-CHH), 1.95–1.93 (m, 1H, 17¹-CHH), 1.88–1.83 (m, 2H, CH₂-hexyl), 1.55–1.49 (m, 5H, 8-CH₂CH₃ & -CH₂-hexyl), 1.45–1.37 (m, 4H, 2CH₂-hexyl), 1.34 (d, 3H, 18-CH₃, J = 7.2 Hz), 0.93 (t, 3H, CH₃-hexyl, J = 6.8 Hz). EIMS (*m/z*): 741 (M⁺+Na). HRMS: calcd. For C₄₀H₄₅N₅NiO₄: 717.2825. Found: 717.2815.

Ni(II) Mesopurpurin-18-N-hexylimide methyl ester 3

Ni(II)-3-(Vinyl)-purpurin-N-hexylimide **2** (350.0 mg, 0.48 mmol) was dissolved in 100 ml distilled THF. Pd/C (10% w/w, 350.0 mg) and 5–6 drops of triethylamine were added to reaction mixture. The reaction mixture was degassed and flushed with H₂ and stirred vigorously for 12 hr under H₂ atm. Progress of the reaction was monitored by UV-vis and ¹H NMR. After completion of the reaction, the mixture was degassed and flushed with N₂ and filtered over a Celite® bed. The filtrate was concentrated and the crude product purified over a silica column using a 0.5–1% acetone/dichloromethane mixture as eluent. Yield: 300.0 mg (85.4%). UV-vis λ_{max} (in CH₂Cl₂): 661 nm (ϵ 3.2 × 10⁴), 544 nm (ϵ 0.4 × 10⁴), 501 nm (ϵ 0.4 × 10⁴), 419 nm (ϵ 6.0 × 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 8.99 (s, 1H, meso-H), 8.61 (s, 1H, meso-H), 7.86 (s, 1H, meso-H), 4.78 (dd, 1H, 17-H, J = 3.2 & 9.2 Hz), 4.27 (m, 2H, N-CH₂-hexyl), 4.03 (q, 1H, 18-H, J = 7.2 Hz), 3.60 (s, 3H, CO₂Me), 3.48 (s, 3H, ring-CH₃), 3.44–3.36 (m, 4H, 3-CH₂CH₃ & 8-CH₂CH₃), 2.95 (s, 3H, ring-CH₃), 2.87 (s, 3H, ring-CH₃), 2.64–2.54 (m, 2H, 17²-CH₂), 2.20–2.18 (m, 1H, 17¹-CHH), 1.94–1.92 (m, 1H, 17¹-CHH), 1.87–1.82 (m, 2H, CH₂-hexyl), 1.55–1.48 (m, 8H, 3-CH₂CH₃, 8-CH₂CH₃ & CH₂-hexyl), 1.44–1.36 (m, 4H, 2CH₂-hexyl), 1.33 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.92 (t, 3H, CH₃-hexyl, J = 7.2 Hz). EIMS (*m/z*): 721 (M⁺+H). HRMS: calcd. For C₄₀H₄₇N₅NiO₄: 719.2982. Found: 719.2971.

Ni(II)-20-meso-Formyl mesopurpurin-18-N-hexylimide methyl ester 4

In a two necked 100 ml dry RBF, N,N'-Dimethylformamide (1.0 ml) was dissolved in dry dichloromethane (20.0 ml) and resultant mixture was cooled to 0 °C under N₂ atm. To this cooled mixture, POCl₃ (1.0 ml) was added slowly via syringe under continuous stirring. The reaction mixture was stirred for 20 min at the same temperature and then allowed to warm to room temperature. After 10 min, Ni-(meso)-purpurin-N-hexylimide **3** (100.0 mg, 0.13 mmol) in dry dichloromethane (15.0 ml) was added via syringe and the resultant mixture was stirred for 36 hr at room temperature. The reaction mixture was again cooled to 0 °C and saturated Na₂CO₃ was added dropwise to the solution which was stirred for another 8 hr. The reaction mixture was then extracted with dichloromethane (3 × 50.0 ml) and the organic layers were collected, combined and washed with water (100.0 ml). The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated. The crude product thus obtained was purified over silica column using 1–2% acetone/dichloromethane as eluent. Yield: 85.0 mg (82.5%). UV-vis λ_{max} (in CH₂Cl₂): 685 nm (ϵ 3.4 × 10⁴), 426 nm (ϵ 3.5 × 10⁴), 389 nm (ϵ 4.6 × 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 10.85 (s, 1H, -CHO), 8.70 (s, 1H, meso-H), 8.38 (s, 1H, meso-H), 4.80 (q, 1H, 17-H, J = 6.8 Hz), 4.53 (dd, 1H, 18-H, J = 4.8 & 8.8 Hz), 4.18 (q, 2H, N-CH₂-Hexyl, J = 6.8 Hz), 3.63 (s, 3H, CO₂Me), 3.34 (s, 3H, ring-CH₃), 3.25 (m, 4H, 3-CH₂CH₃ and 8-CH₂CH₃), 2.83 (s, 3H, ring-CH₃), 2.82 (s, 3H, ring-CH₃), 2.64 (m, 2H, 17²-CH₂), 2.17 (m, 1H, 17¹-CH₂), 1.88 (m, 1H, 17¹-CH₂), 1.77 (m, 2H, CH₂-Hexyl), 1.50–1.43 (m, 8H, 3-CH₂CH₃, 8-CH₂CH₃ and CH₂-Hexyl), 1.37 (m, 4H, 2CH₂-Hexyl), 1.14 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.90 (t, 3H, CH₃-Hexyl, J = 6.4 Hz). EIMS (*m/z*): 771 (M⁺+Na). HRMS: calcd. For C₄₁H₄₇N₅NiO₅: 747.2931. Found: 747.2922.

Ni(II)-20-(2-Formylvinyl)mesopurpurinimide-N-hexylimide methyl ester 5

In a two necked 100 ml dry round bottom flask, 3-(dimethylamino)-acrolein (1.0 ml) was dissolved in dry dichloromethane (20.0 ml) and the resultant mixture cooled to 0 °C under N₂ atm. To this cooled mixture, POCl₃ (1.0 ml) was added slowly via a syringe under continuous stirring. The reaction mixture was stirred for 20 min at the same temperature and allowed to warm to room temperature. After 10 min, Ni(II)-mesopurpurin-N-hexylimide **3** (100 mg, 0.13 mmol) in dry dichloromethane (15.0 ml) was added via syringe and the resultant mixture was stirred for 36 hr at room temperature. The reaction mixture was again cooled to 0 °C, a saturated solution of Na₂CO₃ was added dropwise and stirred for another 8 hr. The reaction mixture was then extracted with dichloromethane (3 × 50.0 ml), the organic layers collected, combined and washed with water (100.0 ml). The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated. The crude product thus obtained was purified over a silica column using 1–2% acetone/dichloromethane as eluent. Yield: 80.0 mg (74.7%). UV-vis λ_{max} (in CH₂Cl₂): 690 nm (ϵ 3.4 × 10⁴), 570 nm (ϵ 0.5 × 10⁴), 414 nm (ϵ 5.7 × 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 9.76 (d, 1H, -CHO), 8.78 (s, 1H, meso-H), 8.48 (s, 1H, meso-H), 8.34 (d, 1H, 20¹-CH, J = 15.2 Hz), 5.81 (dd, 1H, 20²-CH, J = 7.6 and 15.6 Hz), 4.55 (dd, 1H, 17-H, J = 3.6 and 8.8 Hz), 4.35 (q, 1H, 18-H, J = 6.8 Hz), 4.21 (q, 2H, N-CH₂-hexyl, J = 6.8 Hz), 3.65 (s, 3H, CO₂Me), 3.40 (s, 3H, ring-CH₃), 3.38–3.26 (m, 4H, 3-CH₂CH₃ and 8-CH₂CH₃), 2.88 (s, 3H, ring-CH₃), 2.70–2.65 (m, 5H, ring-CH₃, 17²-CH₂), 2.22 (m, 1H, 17¹-CHH), 2.01 (m, 1H, 17¹-CHH), 1.81 (m, 2H, CH₂-hexyl), 1.58–1.41 (m, 8H, 3-CH₂CH₃, 8-CH₂CH₃ & CH₂-hexyl), 1.39–1.34 (m, 4H, 2CH₂-Hexyl), 1.19 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.93 (t, 3H, CH₃-Hexyl, J = 7.2 Hz). EIMS (*m/z*): 797 (M⁺+Na). HRMS: calcd. For C₄₃H₄₉N₅NiO₅: 773.3087. Found: 773.3076.

Benzo-isobacterio-purpurin-18-N-hexylimide methyl ester 6 [TiCl₃(DME)_{1.5} method]

In a two neck dry round bottom flask (RBF) (100 ml), TiCl₃ (153 mg, 1 mmol) was taken, dry DME (5 ml) was added and the solution refluxed for 24 h. To this refluxing solution, zinc-copper alloy (176 mg, 2.5 mmol) was added, and refluxing was continued for 2 more hours. Then, Ni(II)-20-formyl-meso-purpurin-N-hexylimide **4** (40.0 mg, 0.052 mmol) in 10 ml of dry DME was added slowly via syringe to the reaction mixture and the entire mixture was stirred for 45 min at same temperature. The mixture was cooled and concentrated to dryness under vacuum. The crude product was dissolved in CH₂Cl₂ and washed with brine solution, organic layer separated, dried and concentrated. The product was purified over silica gel column using 1–3% acetone/CH₂Cl₂ mixture as eluent. Yield: 12 mg (42%) UV-vis λ_{max} (in CH₂Cl₂): 687 nm: ¹H NMR (400 MHz, CDCl₃): δ 8.20 (s, 1H, meso-H), 8.14 (d, 1H, J = 8.4 Hz, Ph-H), 7.66 (d, 1H, J = 6.8 Hz, Ph-H), 7.52 (t, 1H, J = 8.4 Hz, Ph-H), 7.15 (s, 1H, meso-H), 4.50 (m, 1H), 4.11–4.21 (m, 3H), 3.54 (s, 3H, CO₂Me), 3.17 (s, 3H), 2.65 (s, 3H), 2.40–2.46 (m, 1H), 2.32 (q, 2H, J = 7.2 Hz), 1.98–2.01 (m, 1H), 1.75–1.80 (m, 3H), 1.61 (m, 3H), 1.49 (d, 3H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz), 1.38–1.39 (m, 6H), 1.26 (s, 3H), 0.89 (t, 3H, J = 13.2 Hz), 0.26 (t, 3H, J = 7.2 Hz). EIMS (*m/z*): 781 (M+Na). HRMS: calcd. For C₄₃H₄₉N₅NiO₄: 757.3138. Found: 757.3120.

Ni-3-(vinyl)-bis-trifluoromethylbenzyl-purpurinimide (8)

3-(vinyl)-bistrifluoromethylbenzyl-purpurinimide (200.0 mg, 0.25 mmol) was dissolved in 50 ml of toluene and nickel acetylacetonate hydrate (640.0 mg, 2.45 mmol) was added to it. Reaction mixture was reflux vigorously for 2 hr and progress of the reaction was monitored by TLC and UV-vis. After completion, reaction mixture was cooled and directly loaded on a silica column. Product **8** was eluted with 1% acetone/dichloromethane. Yield: 195.0 mg (91.1%). UV-vis λ_{max} (in CH₂Cl₂): 675 nm (ϵ 4.1 × 10⁴), 548 nm (ϵ 0.5 × 10⁴), 423 nm (ϵ 6.9 × 10⁴), 379 nm (ϵ 3.9 × 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 9.00 (s, 1H, meso-H), 8.73 (s, 1H, meso-H), 8.09 (s, 2H, Ph-H), 7.91 (s, 1H, meso-H), 7.78 (s, 1H, Ph-H), 7.55 (dd, 1H, -

$\text{CH}=\text{CH}_2$, $J = 11.6$ & 17.6 Hz), 5.93 (d, 1H, $-\text{CH}=\text{CH}_2$, $J = 10.4$ Hz), 5.91 (d, 1H, $-\text{CH}=\text{CH}_2$, $J = 4.0$ Hz), 5.59 (s, 2H, $\text{N}-\text{CH}_2-\text{Ph}$), 4.72 (m, 1H, 17-H), 4.06 (q, 1H, 18-H, $J = 7.2$ Hz), 3.60 (s, 3H, CO_2Me), 3.49 (s, 3H, ring- CH_3), 3.40 (m, 2H, 8- CH_2CH_3), 2.98 (s, 3H, ring- CH_3), 2.93 (s, 3H, ring- CH_3), 2.63–2.56 (m, 2H, 17²- CH_2), 2.19 (m, 1H, 17¹- CH_2), 1.92 (m, 1H, 17¹- CH_2), 1.50 (t, 3H, 8- CH_2CH_3 , $J = 7.2$ Hz), 1.32 (d, 3H, 18- CH_3 , $J = 6.8$ Hz). EIMS (m/z): 861 (M+H). HRMS: calcd. For $\text{C}_{43}\text{H}_{37}\text{F}_6\text{N}_5\text{NiO}_4$: 859.2103. Found: 859.2107.

Meso-Ni- bis-trifluoromethylbenzyl-purpurinimide (9)

Ni-3-(vinyl)-bis-trifluoromethylbenzyl-purpurinimide (300.0 mg, 0.34 mmol) was dissolved in 100 ml distilled THF. Pd/C (10% w/w, 600.0 mg) and 5–6 drops of triethylamine were added to reaction mixture. Reaction mixture was flushed with H_2 and stirred vigorously for 12 hr under H_2 atm. Progress of the reaction was monitored by UV-vis and ^1H NMR. After completion, reaction mixture was degassed, flushed with N_2 and filtered over celite® bed. Filtrate was concentrated and crude product was purified over alumina (G-III) column using 0.5–1 % acetone/dichloromethane mixture as eluent. Yield: 280.0 mg (93.1 %). UV-vis λ_{max} (in CH_2Cl_2): 664 nm ($\epsilon 3.2 \times 10^4$), 545 nm ($\epsilon 0.4 \times 10^4$), 420 nm ($\epsilon 6.0 \times 10^4$). ^1H NMR (400 MHz, CDCl_3): δ 8.98 (s, 1H, meso-H), 8.59 (s, 1H, meso-H), 8.08 (s, 2H, Ph-H), 7.85 (s, 1H, meso-H), 7.77 (s, 1H, Ph-H), 5.58 (s, 2H, $\text{N}-\text{CH}_2-\text{Ph}$), 4.71 (dd, 1H, 17-H, $J = 3.60$ & 8.80 Hz), 4.04 (q, 1H, 18-H, $J = 7.2$ Hz), 3.58 (s, 3H, CO_2Me), 3.46 (s, 3H, ring- CH_3), 3.42–3.34 (m, 4H, 3- CH_2CH_3 & 8- CH_2CH_3), 2.94 (s, 3H, ring- CH_3), 2.86 (s, 3H, ring- CH_3), 2.62–2.55 (m, 2H, 17²- CH_2), 2.16–2.13 (m, 1H, 17¹- CH_2), 1.93–1.89 (m, 1H, 17¹- CH_2), 1.55–1.48 (m, 6H, 3- CH_2CH_3 & 8- CH_2CH_3), 1.32 (d, 3H, 18- CH_3 , $J = 6.8$ Hz). EIMS (m/z): 863 (M+H). HRMS: calcd. For $\text{C}_{43}\text{H}_{39}\text{F}_6\text{N}_5\text{NiO}_4$: 861.2260. Found: 861.2263.

Benzo-isobacterio-purpurin-18-N-(3, 5-trifluoromethyl-benzyl)imide methyl ester 11 [TiCl_3 (DME)_{1.5} method]

Yield: 29 mg (36%) UV-vis λ_{max} (in CH_2Cl_2): 609 nm: ^1H NMR (400 MHz, CDCl_3): δ 8.78 (s, 1H, meso-H), 8.46 (s, 1H, meso-H), 8.31 (d, 1H, 20¹-CH, $J = 15.2$ Hz), 8.03 (s, 2H, Ph-H), 7.77 (s, 1H, Ph-H), 5.80 (dd, 1H, 20²-CH, $J = 7.6$ & 15.6 Hz), 5.52 (s, 2H, benzylic- CH_2), 4.49 (dd, 1H, 17-H, $J = 4.0$ and 8.8 Hz), 4.32 (q, 1H, 18-H, $J = 7.2$ Hz), 3.63 (s, 3H, CO_2Me), 3.38 (s, 3H, ring- CH_3), 3.35–3.27 (m, 4H, 3- CH_2CH_3 and 8- CH_2CH_3), 2.87 (s, 3H, ring- CH_3), 2.66 (s, 3H, ring- CH_3), 2.64–2.61 (m, 2H, 17²- CH_2), 2.18 (m, 1H, 17¹- CH_2), 2.00 (m, 1H, 17¹- CH_2), 1.47 (t, 3H, 8- CH_2CH_3 , $J = 7.2$ Hz), 1.46 (t, 3H, 3- CH_2CH_3 , $J = 7.2$ Hz), 1.16 (d, 3H, 18- CH_3 , $J = 6.8$ Hz). EIMS (m/z): 921 (M+Na). HRMS: calcd. For $\text{C}_{46}\text{H}_{41}\text{F}_6\text{N}_5\text{NiO}_4$: 899.2416. Found: 899.2408.

Dihydrobenzo-isobacterio-purpurin-18-N-(3, 5-trifluoromethyl-benzyl)imide methyl ester 12 [TiCl_3 (DME)_{1.5} method]

Yield: 35 mg (44%) UV-vis λ_{max} (in CH_2Cl_2) 663: ^1H NMR (400 MHz, CDCl_3): δ 8.26 (s, 1H, meso-H), 8.00 (s, 2H, Ph-H), 7.74 (s, 1H, meso-H), 7.20 (s, 1H, Ph-H), 6.82 (dd, 1H, 20¹-CH, $J = 3.2$ & 9.6 Hz), 6.08 (m, 1H, 20¹-CH), 5.47 (s, 2H, benzylic- CH_2), 4.63 (dd, 1H, 17-H, $J = 3.6$ & 8.4 Hz), 3.56 (q, 1H, 18-H, $J = 6.8$ Hz), 3.55 (s, 3H, CO_2Me), 3.15 (s, 3H, ring- CH_3), 3.13–3.11 (m, 3H, 8- CH_2CH_3 and 3-CH), 2.85–2.82 (dd, 1H, 20³-CHH, $J = 6.4$ & 16.4 Hz), 2.63–2.60 (dd, 1H, 20³-CHH, $J = 6.4$ and 16.4 Hz), 2.58 (s, 3H, ring- CH_3), 2.42–2.35 (m, 2H, 3- CHHCH_3 and 17²-CHH), 2.27 (m, 1H, 17²-CHH), 2.10 (m, 1H, 3- CHHCH_3), 2.07 (m, 1H, 17¹-CHH), 1.85 (m, 1H, 17¹-CHH), 1.82 (s, 3H, 2- CH_3), 1.39 (t, 3H, 8- CH_2CH_3 , $J = 7.6$ Hz), 1.35 (t, 3H, 3- CH_2CH_3 , $J = 7.2$ Hz), 1.28 (d, 3H, 18- CH_3 , $J = 7.2$ Hz). EIMS (m/z): 923 (M+Na). HRMS: calcd. For $\text{C}_{46}\text{H}_{43}\text{F}_6\text{N}_5\text{NiO}_4$: 901.2573. Found: 901.2565.

1,2-Bis [nickel (II)-mesopurpurin-18-N-hexylimide]ethane 13

In a two neck dry RBF (100 ml), dry THF (15 ml) and zinc metal (16.78 mg, 0.25 mmol) were taken and refluxed under N₂ atm. To this refluxing solution was added dropwise TiCl₄ (1M sol. in toluene, 0.128 ml, 0.128 mmol) and the resulting mixture was stirred for 2 hr under reflux. After 2 hr, Ni(II)-20-formyl-meso-purpurin-N-hexylimide **4** (48.0 mg, 0.064 mmol) in 10 ml of dry THF was added slowly via a syringe and the reaction mixture was further stirred for 45 min at same temperature. The mixture was then cooled and concentrated to dryness under vacuum. The crude product was dissolved in CH₂Cl₂ and washed with a brine solution, the organic layer was separated, dried and then concentrated. The product was purified over a silica gel column using 1–3% acetone/DCM mixture as eluent. Yield: 20.0 mg (42.5 %). UV-vis λ_{max} (in CH₂Cl₂): 687 nm (ϵ 5.3 $\times$ 10⁴), 426 nm (ϵ 9.4 $\times$ 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 8.85 (s, 1H, meso-H), 8.55 (s, 1H, meso-H), 7.09 (s, 1H, 20¹-CH), 4.53 (dd, 1H, 17-H, J = 3.6 & 8.8 Hz), 4.32 (q, 1H, 18-H, J = 7.2 Hz), 4.21 (q, 2H, N-CH₂-Hexyl, J = 6.8 Hz), 3.62 (s, 3H, CO₂Me), 3.43 (s, 3H, ring-CH₃), 3.41–3.33 (m, 4H, 3-CH₂CH₃ & 8-CH₂CH₃), 2.94 (s, 3H, ring-CH₃), 2.71 (s, 3H, ring-CH₃), 2.69–2.63 (m, 2H, 17²-CH₂), 2.24 (m, 1H, 17¹-CHH), 2.06 (m, 1H, 17¹-CHH), 1.81 (m, 2H, CH₂-Hexyl), 1.52–1.43 (m, 8H, 3-CH₂CH₃, 8-CH₂CH₃ & CH₂-Hexyl), 1.39–1.31 (m, 4H, 2CH₂-Hexyl), 1.09 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.90 (t, 3H, CH₃-Hexyl, J = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 173.9, 166.5, 162.8, 160.3, 156.7, 149.6, 148.9, 146.1, 143.5, 143.3, 141.1, 139.1, 139.0, 136.1, 135.9, 133.6, 133.3, 120.6, 109.0, 108.2, 104.7, 97.6, 54.3, 51.6, 46.8, 39.8, 32.3, 31.7, 29.7, 28.8, 27.3, 27.0, 22.7, 19.5, 19.0, 17.0, 16.6, 15.7, 14.1, 12.2, 10.5. EIMS (*m/z*): Positive mode: 1488 (M⁺+Na), Negative mode: 1464 (M⁻-H). HRMS: calcd. For C₈₂H₉₄N₁₀Ni₂O₈: 1462.5963. Found: 1462.5953.

Trans-, trans-, trans-1,6-Bis[nickel(II)mesopurpurin-18-N-hexylimide methyl ester-1,3,5-hexatriene] 15

In a two neck dry round bottom flask (100 ml), dry THF (15 ml) and zinc metal (16.78 mg, 0.25 mmol) were taken and refluxed under N₂ atm. To this refluxing solution was added dropwise TiCl₄ (1M sol. in toluene, 0.129 ml, 0.129 mmol) and the resultant mixture was stirred for 2 hr under reflux. After 2 hr, Ni(II)-20-vinylformyl-mesopurpurin-N-hexylimide **5** (50.0 mg, 0.064 mmol) in 10 ml of dry THF was added slowly via a syringe and the reaction mixture was further stirred for 45 min at the same temperature. The reaction mixture was cooled and concentrated to dryness under vacuum. The crude sample was dissolved in dichloromethane and washed with brine solution, the organic layer separated, dried and concentrated. The product was purified over a silica gel column using 1–3% acetone/CH₂Cl₂ mixture as an eluent. Yield: 15.0 mg (30.6%). UV-vis λ_{max} (in CH₂Cl₂): 696 nm (ϵ 5.8 $\times$ 10⁴), 430 nm (ϵ 11.3 $\times$ 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 8.86 (s, 1H, meso-H), 8.56 (s, 1H, meso-H), 7.44 (d, 1H, 20¹-CH, J = 15.2 Hz), 6.45 (dd, 1H, 20²-CH, J = 2.8 and 6.8 Hz), 5.72 (ddd, 1H, 20³-CH, J = 2.8 and 6.8 Hz), 4.50 (dd, 1H, 17-H, J = 3.8 & 9.2 Hz), 4.19 (m, 3H, 18-H and N-CH₂-Hexyl), 3.61 (s, 3H, CO₂Me), 3.42 (s, 3H, ring-CH₃), 3.40–3.35 (m, 4H, 3-CH₂CH₃ and 8-CH₂CH₃), 2.96 (s, 3H, ring-CH₃), 2.79 (s, 3H, ring-CH₃), 2.61 (t, 2H, 17²-CH₂, J = 8.0 Hz), 2.20 (m, 1H, 17¹-CHH), 1.98 (m, 1H, 17¹-CHH), 1.81 (m, 2H, CH₂-hexyl), 1.56–1.41 (m, 8H, 3-CH₂CH₃, 8-CH₂CH₃ & CH₂-hexyl), 1.39–1.33 (m, 4H, 2CH₂-hexyl), 1.03 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.88 (t, 3H, CH₃-hexyl, J = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 173.9, 166.5, 162.8, 160.2, 157.6, 149.5, 149.4, 145.3, 143.6, 143.5, 142.2, 140.8, 139.1, 138.7, 135.8, 134.7, 133.8, 133.1, 129.3, 120.3, 108.8, 107.1, 103.6, 97.8, 53.4, 51.5, 46.7, 39.8, 32.2, 31.7, 29.7, 28.8, 28.0, 27.0, 22.7, 19.0, 18.8, 17.0, 16.7, 16.0, 14.0, 12.2, 10.5. EIMS (*m/z*): Positive mode: 1540 (M⁺+Na), Negative mode: 1516 (M⁻-H). HRMS: calcd. For C₈₆H₉₈N₁₀Ni₂O₈: 1514.6276. Found: 1514.6297.

Ni(II)-3-Formyl-3-devinyl-purpurin-18-N-hexylimide methyl ester 16

To a solution of Ni-purpurin-18-N-hexylimide methyl ester 2 (300 mg, 0.42 mmol) in THF (80 ml) were added a solution of OsO₄ (118 mg, 0.46 mmol) in CCl₄ (20 ml) and a solution of NaIO₄ (1.8 g, 8.4 mmol) in water (50 ml) successively. The mixture was stirred at room temperature for 6 h, diluted with CH₂Cl₂ (300 ml), washed with water and dried with Na₂SO₄. The solvent was removed and the residue was purified with column chromatography on alumina, eluting with 0.5% acetone/CH₂Cl₂ (v/v 40/1) to provide the compound as dark brown plates. Yield: 190 mg (63%). UV-vis λ_{max} (in CH₂Cl₂): 708 nm (ϵ 5.3 $\times$ 10⁴), 565 nm (ϵ 0.6 $\times$ 10⁴), 433 nm (ϵ 6.3 $\times$ 10⁴), 388 nm (ϵ 4.2 $\times$ 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 10.95 (s, 1H, -CHO), 9.69 (s, 1H, meso-H), 9.10 (s, 1H, meso-H), 8.10 (s, 1H, meso-H), 4.82 (d, 1H, 17-H, J = 9.2 Hz), 4.29 (m, 2H, N-CH₂Hexyl), 4.13 (q, 1H, 18-H, J = 7.2 Hz), 3.62 (s, 3H, CO₂Me), 3.54 (s, 3H, ring-CH₃), 3.46 (m, 2H, 8-CH₂CH₃), 3.33 (s, 3H, ring-CH₃), 3.03 (s, 3H, ring-CH₃), 2.66 (m, 1H, 17²-CHH), 2.58 (m, 1H, 17²-CHH), 2.21 (m, 1H, 17¹-CHH), 1.94 (m, 1H, 17¹-CHH), 1.87 (m, 2H, -CH₂-Hexyl), 1.56 (t, 3H, 8-CH₂CH₃, J = 7.6 Hz), 1.52 (m, 2H, -CH₂-Hexyl), 1.41 (m, 4H, -2CH₂-Hexyl), 1.35 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.93 (t, 3H, CH₃-Hexyl, J = 6.8 Hz). EIMS (*m/z*): 743 (M⁺+Na). HRMS: calcd. For C₃₉H₄₃N₅NiO₅: 719.2618. Found: 719.2610.

Ni(II)-3-(2-Formylvinyl)-3-devinyl-purpurin-18-N-hexylimide methyl ester 17

In a two necked 100 ml dry RBF, a mixture of N,N-dimethylformamide (1.0 ml) and dry dichloromethane (20.0 ml) was cooled to 0 °C under N₂ atm. To this cooled mixture, POCl₃ (1.0 ml) was added slowly via syringe under continuous stirring. The reaction mixture was stirred for 20 min at the same temperature and then allowed to warm to room temperature. After 10 min, Ni(II)-3-vinyl-purpurin-N-hexylimide 2 (100.0 mg, 0.13 mmol) in dry dichloromethane (15.0 ml) was added via syringe and the resultant mixture was stirred for 36 hr at room temperature. The reaction mixture was again cooled to 0 °C, a saturated solution of Na₂CO₃ was added dropwise and stirred for another 8 hr. The reaction mixture was then extracted with dichloromethane (3 $\times$ 50.0 ml), the organic layers collected, combined and washed with water (100 ml). It was separated, dried over anhydrous Na₂SO₄ and concentrated. The crude product thus obtained was purified over silica column using 1–2 % acetone/dichloromethane as eluent. Yield: 70.0 mg (67.9%). UV-vis λ_{max} (in CH₂Cl₂): 704 nm (ϵ 4.8 $\times$ 10⁴), 561 nm (ϵ 0.6 $\times$ 10⁴), 427 nm (ϵ 5.2 $\times$ 10⁴), 394 nm (ϵ 4.6 $\times$ 10⁴), 330 nm (ϵ 2.9 $\times$ 10⁴). ¹H NMR (400 MHz, CDCl₃): δ 9.96 (d 1H, -CHO, J = 7.2 Hz), 9.04 (s, 1H, meso-H), 8.74 (s, 1H, meso-H), 8.31 (dd, 1H, 3-CH=CH-CHO, J = 16.0 Hz), 8.03 (s, 1H, meso-H), 6.96 (dd, 1H, 3-CH=CH-CHO, J = 7.6 & 16.0 Hz), 4.78 (dd, 1H, 17-H, J = 2.8 & 9.2 Hz), 4.28 (m, 2H, N-CH₂-Hexyl), 4.12 (q, 1H, 18-H, J = 6.8 Hz), 3.64 (s, 3H, CO₂Me), 3.51 (s, 3H, ring-CH₃), 3.47–3.38 (m, 2H, 8-CH₂CH₃), 3.09 (s, 3H, ring-CH₃), 2.96 (s, 3H, ring-CH₃), 2.71–2.68 (m, 1H, 17²-CHH), 2.63–2.60 (m, 1H, 17²-CHH), 2.25–2.23 (m, 1H, 17¹-CHH), 1.94–1.90 (m, 1H, 17¹-CHH), 1.88–1.85 (m, 2H, CH₂-Hexyl), 1.55–1.49 (m, 5H, 8-CH₂CH₃ & -CH₂-Hexyl), 1.45–1.37 (m, 4H, 2CH₂-Hexyl), 1.34 (d, 3H, 18-CH₃, J = 6.8 Hz), 0.93 (t, 3H, CH₃-Hexyl, J = 6.8 Hz). EIMS (*m/z*): 769 (M⁺+Na). HRMS: calcd. For C₄₁H₄₅N₅NiO₅: 745.2774. Found: 745.2764.

Bis-3-[Ni(II)purpurin-18-N-hexylimide]ethane 18

In a two neck dry RBF (100 ml), dry THF (15 ml) and zinc metal (18.16 mg, 0.27 mmol) were taken refluxed under N₂ atm. To this refluxing solution was added dropwise TiCl₄ (1M sol. in toluene, 0.138 ml, 0.138 mmol) and resultant mixture was stirred for 2 hr under refluxing. After 2 hr, Ni(II)-3-Formyl-3-devinyl-purpurin-N-hexylimide 16 (50.0 mg, 0.069 mmol) in 10 ml of dry THF was added slowly via syringe and the reaction mixture was further stirred for 45 min at the same temperature. It was then cooled and concentrated to dryness under vacuum. The crude product was dissolved in dichloromethane and washed with brine solution, the

organic layer separated, dried/concentrated and purified over a silica gel column using a 1–3% acetone/DCM mixture as eluent. Yield: 16.0 mg (32.7 %). UV-vis λ_{max} (in CH_2Cl_2): 708 nm ($\epsilon 6.3 \times 10^4$), 557 nm ($\epsilon 1.1 \times 10^4$), 422 nm ($\epsilon 11.4 \times 10^4$). ^1H NMR (400 MHz, CDCl_3): δ 9.08 (s, 1H, meso-H), 9.06 (s, 1H, meso-H), 8.15 (s, 1H, meso-H), 8.06 (s, 1H, 3¹-CH), 4.83 (dd, 1H, 17-H, $J = 2.8$ & 8.8 Hz), 4.30 (m, 2H, N-CH₂Hexyl), 4.16 (q, 1H, 18-H, $J = 7.2$ Hz), 3.65 (s, 3H, CO₂Me), 3.53 (s, 3H, ring-CH₃), 3.45 (m, 2H, 8-CH₂CH₃), 3.27 (s, 3H, ring-CH₃), 2.94 (s, 3H, ring-CH₃), 2.70 (m, 1H, 17²-CHH), 2.62 (m, 1H, 17²-CHH), 2.29 (m, 1H, 17¹-CHH), 2.02 (m, 1H, 17¹-CHH), 1.88 (m, 2H, -CH₂-Hexyl), 1.52 (m, 5H, 8-CH₂CH₃, -CH₂-Hexyl), 1.46–1.38 (m, 7H, -2CH₂-Hexyl & 18-CH₃), 0.93 (t, 3H, CH₃-Hexyl, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 173.8, 166.7, 162.8, 162.5, 160.0, 149.4, 145.8, 143.6, 143.5, 141.9, 141.3, 139.6, 139.0, 136.1, 134.1, 133.7, 127.6, 120.4, 108.4, 104.6, 97.8, 95.0, 51.6, 47.6, 40.0, 32.1, 31.7, 29.7, 28.8, 28.7, 27.1, 22.7, 20.9, 19.1, 17.1, 14.1, 12.3, 12.2, 10.8. EIMS (m/z): 1431 ($\text{M}^+ + \text{Na}$). HRMS: calcd. For $\text{C}_{78}\text{H}_{86}\text{N}_{10}\text{Ni}_2\text{O}_8$: 1406.5337. Found: 1406.5325.

Trans-, trans-, trans-1,6-Bis[3-Ni(II)purpurin-18-N-hexylimide methyl ester] 19

In a two neck dry RBF (100 ml), dry THF (15 ml) and zinc metal (17.5 mg, 0.26 mmol) were refluxed under N_2 atm. To this refluxing solution was added dropwise TiCl_4 (1M sol. in toluene, 0.134 ml, 0.134 mmol) and the resultant mixture was stirred for 2 hr under reflux. After 2 hr, Ni-20-vinylformyl-mesopurpurin-N-hexylimide **17** (50.0 mg, 0.067 mmol) in 10 ml of dry THF was added slowly via a syringe and the reaction mixture was further stirred for 30–45 min at the same temperature. The reaction mixture was cooled and concentrated to dryness under vacuum. The crude product was dissolved in DCM and washed with brine solution, the organic layer separated, dried and concentrated. It was purified over silica gel column using 1–3% acetone/ CH_2Cl_2 mixture as eluent. Yield: 15.0 mg (30.6%). UV-vis λ_{max} (in CH_2Cl_2): 715 nm ($\epsilon 6.1 \times 10^4$), 560 nm ($\epsilon 1.5 \times 10^4$), 422 nm ($\epsilon 10.3 \times 10^4$). ^1H NMR (400 MHz, CDCl_3): δ 9.03 (s, 1H, meso-H), 8.83 (s, 1H, meso-H), 7.95 (s, 1H, meso-H), 7.64 (d, 1H, 3¹-CH, $J = 15.2$ Hz), 7.29 (m, 1H, 3²-CH), 7.05 (dd, 1H, 3³-CH, $J = 3.2$ & 7.2 Hz), 4.79 (dd, 1H, 17-H, $J = 2.3$ & 8.8 Hz), 4.28 (m, 2H, N-CH₂-Hexyl), 4.10 (q, 1H, 18-H, $J = 6.8$ Hz), 3.63 (s, 3H, CO₂Me), 3.51 (s, 3H, ring-CH₃), 3.48–3.39 (m, 2H, 8-CH₂CH₃), 3.11 (s, 3H, ring-CH₃), 2.99 (s, 3H, ring-CH₃), 2.67 (m, 1H, 17²-CHH), 2.60 (m, 1H, 17²-CHH), 2.25 (m, 1H, 17¹-CHH), 1.99 (m, 1H, 17¹-CHH), 1.89–1.83 (m, 2H, CH₂-Hexyl), 1.54–1.51 (m, 5H, 8-CH₂CH₃ & CH₂-Hexyl), 1.48–1.41 (m, 4H, 2CH₂-Hexyl), 1.35 (d, 3H, 18-CH₃, $J = 6.8$ Hz), 0.92 (t, 3H, CH₃-Hexyl, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 173.8, 166.7, 162.8, 162.5, 160.0, 149.6, 145.6, 143.5, 142.0, 140.7, 139.8, 135.6, 135.5, 134.0, 133.2, 125.1, 121.0, 108.3, 105.0, 94.9, 51.5, 47.5, 43.9, 39.9, 32.1, 31.7, 29.7, 29.5, 29.3, 28.8, 28.7, 27.1, 22.7, 20.9, 19.1, 17.1, 16.8, 14.1, 12.3, 12.3, 10.8. HRMS: calcd. For $\text{C}_{82}\text{H}_{90}\text{N}_{10}\text{Ni}_2\text{O}_8$: 1458.5650. Found: 1458.5641.

Electrochemical and Spectroelectrochemical Measurements

Cyclic voltammetry (CV) measurements were performed at 298K on an EG&G model 173 potentiostat coupled with an EG&G model 175 universal programmer in deaerated benzonitrile (PhCN) solution containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. A three-electrode system was utilized and consisted of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. Thin-layer spectroelectrochemical measurements were carried out using an optically transparent platinum thin-layer working electrode and a Hewlett-Pachard model 8453 diode array spectrophotometer coupled with an EG&G model 173 universal programmer.

Molecular Modeling Computational Method

The 3D structures of the monomer units (**4** and **16**) were modeled from the crystal structure of anhydrosorhodoisobacteriochlorin methyl ester-nickel(ii)³¹ as a template. Appropriate modifications including changes of atoms and bond types, deletions and additions of atoms and bonds, were performed with the SYBYL molecular modeling program version 8.0 (Tripos Inc., St. Louis, MO) using standard geometry. An extended conformation was assumed for the n-hexyl tail. The dimers **13**, **14** and **15** were modeled from the monomer unit **4** with assumed linker conformations as shown in Scheme 2. Similarly, the dimers **18**, **19** and **19a** were modeled from the monomer unit **16** as shown in Scheme 3. The geometry of each compound was first optimized with a molecular mechanics method using an MMFF force field which was followed by a full optimization with a semiempirical molecular orbital method, PM3, both with the SPARTAN (Wavefunction Inc., Irvine, CA) software. The default parameters were used except mmOK option with PM3 optimization.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The financial support from the NIH (CA55791, CA127369), Roswell Park Alliance Foundation and the Robert A. Welch Foundation (K.M.K., Grant E-680) is gratefully acknowledged. Mass spectrometry analyses were performed at the Biopolymer Facility, Roswell Park Cancer Institute, Buffalo and the Michigan State University, East Lansing, Michigan. Dr. M. P. Dobhal is thankful to Dr. N. K. Jain, Vice –Chancellor, University of Rajasthan, Jaipur, India for the study-leave award.

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Figure 1.
Partial NMR spectra of benzoisobacteriopurpurinimides **11** and **12**

Figure 2. Energy optimized structures of (A) dimer **14** containing a *trans-cis-trans* and (B) dimer **15**, containing a *trans-trans-trans* hexatriene linker.

Figure 3. Energy minimized structures of β - β -linked dimers with a hexatriene linker: (A) *trans-trans-trans*- configuration **19** and (B) *trans-cis-trans*- configuration **19a**.

Figure 4. Cyclic voltammograms of monomeric chlorin **3** and dyads with “short” (**13**) or “long” (**15**) meso linkers and “short” (**18**) or “long” (**19**) β -pyrrole linkers in PhCN containing 0.1 M TBAP. Scan rate = 0.10 V/s.

Monomeric Chlorin 3

Figure 5. UV-visible spectral changes of compound **3** in PhCN containing 0.2 M TBAP during a) the first reduction and b) the first oxidation processes. The solid lines correspond to the absorption spectra of the neutral compounds.

Figure 6.

UV-visible spectral changes during a global one electron reduction of the four dyads at an applied potential of -1.10 V in PhCN containing 0.2 M TBAP. The solid lines correspond to the absorption spectra of the neutral compounds.

Figure 7. UV-visible spectral changes during a global one electron oxidation of the four dyads at an applied potential of 1.00 to 1.10 V in PhCN containing 0.2 M TBAP. The solid lines correspond to the absorption spectra of the neutral compounds.

Scheme 1.
Synthesis of *meso*-substituted formyl and 2-formylvinyl purpurinimides

Scheme 2.

Intramolecular cyclization of the 20-*meso*-2-formylvinylpurpurinimide under the McMurry reaction conditions using $\text{TiCl}_3(\text{DME})_{1.5}\text{-Zn}(\text{Cu})$ combination.

Scheme 3.

Synthesis of carbon-carbon linked purpurinimide dimers *via* modified McMurry reaction using (TiCl_4/Zn combination).

Scheme 4.
 β - β -linked purpurinimides with one and three double bonds

Table 1
Half-wave potentials (V vs SCE) of investigated nickel chlorins in PhCN, 0.1 M TBAP.

Cpd	Linker ^a		Oxidation		Reduction		HOMO-LUMO ^b
	position	"type"	2 nd	1 st	1 st	2 nd	
3		none	1.11	0.81	-0.99	-1.43	1.80
13	meso	short	1.19	0.84	-0.85	-1.42	1.69
18	β	short	1.14	0.87	-0.84	-1.30	1.71
15	meso	long	1.20	0.88	0.70	-1.39	1.62
19	β	long	1.16	0.83	0.76	-1.24	1.65

^a see schemes 1, 3 and 4 for structures

^b $\Delta E_{1/2}$ between first reduction and first oxidation

Table 2
UV-visible spectral data of neutral nickel chlorins in PhCN containing 0.1 M TBAP.

Linker	Cpd	λ_{max} , nm ($\epsilon \times 10^{-4}$, mol ⁻¹ cm ⁻¹)			
		Soret region		Visible region	
none	3	393 (3.5)	421 (6.1)	544 (0.4)	615 (0.95)
	13	363 (4.9)	429 (10.9)	581 (1.1)	695 (6.3)
β -pyrrole	15	363 (2.8)	431 (6.6)	581 (0.8)	700 (3.6)
	18	392 (8.6)	424 (13.1)	556 (1.4)	677 (5.5)
	19	391 (5.1)	425 (8.7)	560 (1.3)	683 (3.8)
					716 (5.3)