

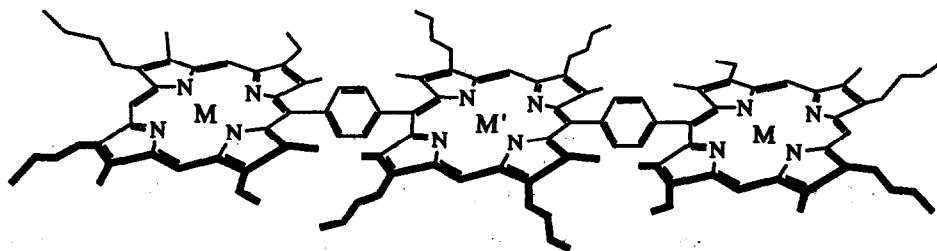
SELECTIVE INSERTION OF Ni(II) INTO THE OUTER PORPHYRIN SUBUNITS OF A TRIMERIC PORPHYRIN ARRAY

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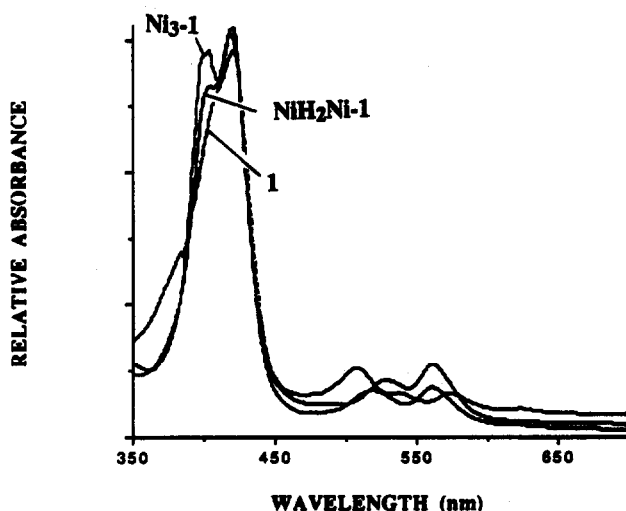
Abstract: The selective insertion of Ni(II) into the outer porphyrin subunits of a phenyl-linked trimeric porphyrin array allows for the examination, by steady-state absorption, of the relative contributions of the transition dipoles to the overall electronic coupling between the porphyrin macrocycles.

The optical properties of linked porphyrin arrays are of interest in terms of the electronic coupling between the porphyrin subunits. Spectral shifts associated with subunit coupling have been described previously in terms of Kasai's molecular excitation model¹ and applied to phenyl-linked porphyrins by Freisner and Sessler² and recently by Maruyama,³ McLendon,⁴ and others.⁵ We have been interested in the effect of electronic coupling between porphyrin subunits in donor-acceptor systems⁶ in which the photoinduced electron transfer reactions are governed by the porphyrin-porphyrin interactions. In order to gain further insight into the specific nature of the electronic interactions within these systems, we required systems containing metal cation(s) selectively complexed to one or more of the macrocycle subunits. Herein we report the preparation and static absorption properties of such a system incorporating Ni(II) into the outer porphyrin subunits of a trimeric array, NiH₂Ni-1, as well as its fully-metallated, Ni₃-1, and metal-free, 1, ^{6b} isomers.



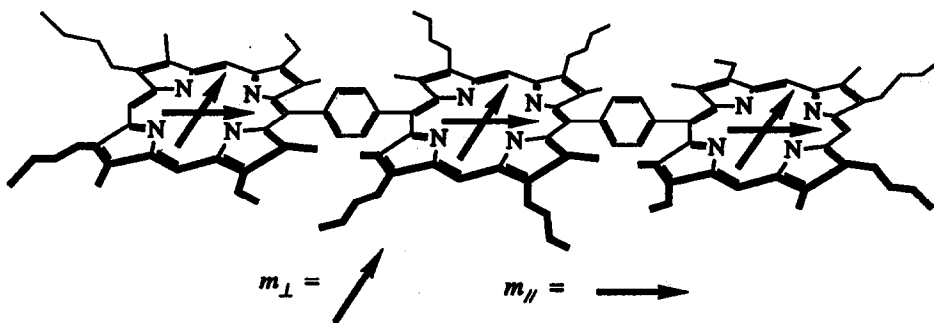
1. M = M' = H₂
Ni₃-1. M = M' = Ni₃
NiH₂Ni-1. M = Ni; M' = H₂

The choice of Ni(II) was dictated by the need to follow the regiochemistry of metallation by NMR spectroscopy. Thus, it was necessary to use a diamagnetic metal cation. So as to avoid the problems associated with the separation of metallated regioisomers, a further requirement was that the metallation reaction proceed slowly enough to afford a sufficient degree of selectivity. Nickel(II), in the form of NiCl₂, fulfilled both of these requirements. In the event, two equivalents of NiCl₂ were introduced to a 5% MeOH/CHCl₃ solution of **1** (containing a trace of NaOAc) and heated at reflux until no further changes could be observed by TLC and UV-vis spectroscopy (see Experimental Section). The desired selectively metallated trimer, NiH₂Ni-**1**, was isolated by chromatography on silica gel (45% yield) along with traces of uncharacterized regiometallated isomers as well as the fully metallated Ni₃-**1** and unreacted **1**. The identity of NiH₂Ni-**1**, containing metal cations in the outer porphyrin macrocycles, was confirmed by the combination of FAB-MS and ¹H NMR spectroscopy. The 300 MHz ¹H NMR spectrum in the *meso* and phenyl regions for this compound unambiguously revealed the indicated regiochemistry of metallation. For instance, the 2' and 3' positions of the linking phenyl groups, which resonate as a singlet in both **1** and Ni₃-**1**, appear as a doublet of doublets in the 8.24-8.40 ppm region in the case of NiH₂Ni-**1** (c.f. Experimental Section).



Excitonic interactions are more pronounced for the fully metallated, Ni₃-**1**, and selectively metallated, NiH₂Ni-**1**, systems than for the unmetallated trimer **1**. The absorption spectra for these compounds in CHCl₃ (see above) exhibit splitting in the Soret region ($\lambda_{\text{max}} = 402, 420$ nm for NiH₂Ni-**1** and $\lambda_{\text{max}} = 405, 419$ nm for Ni₃-**1**). These splittings depend upon the interporphyrin

angles and the direction of the transition dipole moments of the monomer subunits. In the case of phenyl-linked porphyrins, two degenerate Soret transitions ($B_{//}$ and B_{\perp}) with $m_{//}$ and m_{\perp} being the corresponding transition dipoles must be considered. According to the theory, $B_{//}$ will be red-shifted and B_{\perp} blue-shifted, due to the head-to-tail and face-to-face orientations of $m_{//}$ and m_{\perp} , respectively. The result is a split in the Soret band. Notably, the selectively metallated system, $\text{NiH}_2\text{Ni-1}$, gives rise to a split Soret with diminished intensity for the blue-shifted component. The intensity of the transition due to the head-to-tail dipole interaction (the red-shifted component) is unaffected by the absence of Ni(II) in the central porphyrin indicating that the presence of the metal cation may only serve to perturb the face-to-face dipole. Although further experimental support is lacking, this phenomenon may be unique to the phenyl linkage or may be a general property of coupled porphyrins. The preparation of selectively metallated systems such as $\text{NiH}_2\text{Ni-1}$ permits this aspect of electronic coupling to be examined.



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EXPERIMENTAL SECTION:

$\text{NiH}_2\text{Ni-1}$. A 50 mL round-bottomed flask was charged with 25 mg $16^{(b)}$ (0.013 mmol), 6.6 mg NiCl_2 (0.026 mmol, 2 eq.) and 20 mL 5% $\text{MeOH}/\text{CHCl}_3$ (v/v) and heated at reflux. After 6 hours, TLC (silica gel, 2% $\text{MeOH}/\text{CHCl}_3$) indicated the complete conversion of starting material to products. The solvent was removed *in vacuo* and the reaction mixture loaded onto a silica gel column. The desired product was eluted with 2% $\text{MeOH}/\text{CHCl}_3$ (R_f 0.8, under conditions where the R_f of Ni_3-1 and 1 are ca. 1.0 and 0.4, respectively) and purified further by recrystallization from CHCl_3 /hexane (Yield 45%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ -1.59 (2H, br. s, NH); 1.12 (12H, t (J = 7.34 Hz), 2,8,12,18- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.18 (12H, t (J = 7.36 Hz), 13",17"- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.69-1.96

(16H, m, 2,8,12,18,13",17"-CH₂CH₂CH₂CH₃); 1.77 (8H, t (J = 7.42 Hz), 2",8"-CH₂CI-I~); 2.1@ (SH, quintet, 13",17"-C"I-I₂CI-I~CH₂CH₃); 2.29 (SH, quintet, 2,8,12,18-CH₂CH~CH₂CH₃); 3.00 (12H, s, 3,7,13,17-CH₃); 3.06 (12H, s, 3",7"-CH₃); 3.44 (12H, s, 12",18"-CH₃); 3.85 (8I-I, t (J = 7.46 Hz), 13",17,-CH~CH₂CH₂CH₃); 3.95 (SH, q (J = 7.63 Hz), 4.12 (SH, t (J ffi 6.72), 2,8,12,18-CI-I~CH₂CHaCH₃); 8.24-8.40 (SH, dd (J ffi 7.69 Hz), 2',3'-H); 9.53 (2I-I,s, 15"-H); 9.64 (4H, s, 10",20,'-H); 10.38 (2H, s, 10,20-H) ppm. Mass Spectrum (FAB, 70 eV) m/z (relative intensity, %) 1922 (M+ + 2H, 51%); 1921 (M+ + H, 100%); 1920 (M+, 36%). Exact Mass for C124I-II47NI2Ni2: talc. 1920.0579, obsd. 1920.0549.

Ni3-L The fully metallated isomer was prepared following the procedure above using an excess of NiCl₂ (0.19 nm~l NiCl₂for 0.014 mmol of 1). The yield of the metallated pmdact as a bright pink solid was essentially quantitative. ¹HNMR (300 MHz, CDCl₃) 8 1.12 (12I-I, t (J = 7.28 Hz), 13", 17"-CH₂CH₂CH₂CH₃); 1.13 (12H, t (J ffi 7.31 Hz), 2, 8, 12, 18-CH₂CH₂CH₂C/~); 1.72 (12H, t (J ffi 7.39 Hz), 2", 8"-CH₂CH₃); 1.77 (16I-I, m, 2, 8, 1, 18, 13", 17"-CH₂CH₂CI-I~CH₃); 2.10 (8I-I, quintet (J ffi 7.7 Hz), 13", 17"-CH₂CI-I~CH₂CH₃); 2.18 (SH, quintet (J = 7.38 Hz), 2, 8, 12, 18-CH₂CI-I~CH₂CH₃); 2.83 (12H, s, 3, 7, 13, 17-CH₃); 2.86 (12H, s, 3", 7"-CH₃); 3.43 (12H, s, 12", 18"-CH₃); 3.77 (8I-I, t (J ffi 7.62 Hz), 13", 17"-CH₂CH₂CH₂CH₃); 3.85 (8H, t (J = 7.63 Hz), 2", 8"-CH₂CH₂CH₂CH₃); 3.86 (8H, t (J ffi 7.04), 2, 8, 12, 18-CH₂CH₂CH₂CH₃); 8.17 '(SH, s, 2', 3', 5', 6'-H), 9.49 (2H, s, 15"-H); 9.53 (2H, s, 10, 20-H); 9.61 (4H, s, 10", 20"-H) ppm. Mass Spectrum (FAB, 70 eV) m/z (relative intensity, %) 1974 (M+, 46); 1975 (M+ + 1, 48); 1976 (M+ + 2, 66); 1977 (M+ + 3, 62); 1978 (M+ + 4, 100); 1979 (M+ + 5, 89); 1980 (M+ + 6, 59). Exact Mass for C124H144N12Ni3: calc. 1974.9696, obsd. 1975.1535.

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