Table I. Fluorescence Parameters for the Cyanine Dye I in Methanol and Surfactant Micelles

medium	ϕ_F	λ_{max}, nm	η^{25}, cP	ϵ^a
methanol	0.09	510	0.547	32.6
NaLS-water	0.45	517	±30	
$Mg(LS)_2$-water	0.54	518		
$Cd(LS)_2$-water	~0.7	518		
water	~0.03	506	0.89	78.5
glycerol	0.82	514	954	42.5

[a] Dielectric constant.

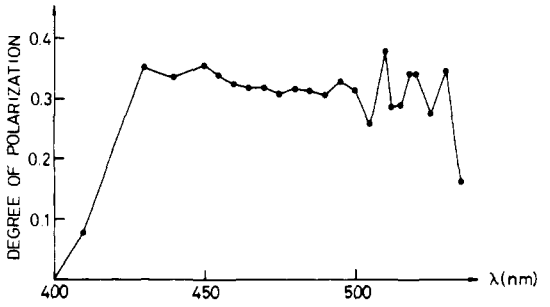

Figure 2. Polarization spectrum of a solution of 10^{-6} M cyanine in 10^{-2} M aqueous NaLS.

surface region, the rest protruding into the micellar interior. Internal molecular motion of the cyanine will be controlled by the local microviscosity which is significantly higher in the surfactant assembly than in methanol.[6] Thus, conformational changes along the polymethine chain leading to radiationless deactivation are retarded and the fluorescence quantum yield is increased. This is corroborated by the high ϕ_F (= 0.82) found for I in a high viscosity medium like glycerol (η^{25} = 954 cP). Furthermore, the nature of the counterion affects the fluorescence behavior (Table I). The replacement of the sodium counterion by either Mg^{2+} or Cd^{2+} ions induces a further increase in the quantum yield. The effect of Mg^{2+} or Cd^{2+} is to contract adjacent head groups of the monomer surfactant units which leads to further immobilization of the dye by an effective increase in viscosity.[6]

A direct means to investigate the rotational motion of excited states is provided by fluorescence polarization measurements. The degree of polarization is defined as[7]

$$p = (I_{II} - I_I)/(I_{II} + I_I) \quad (1)$$

where I_{II} and I_I refer to the emission intensity measured with parallel and crossed polarizers, respectively, and corrected for instrumental artifacts. Figure 2 shows a polarization spectrum of I in NaLS micellar solution. The value of p varies between 0.3 and 0.4 for most of the excitation wavelengths in the first absorption band. The degree of polarization is related to the rotational correlation time τ_R. If the absorption and emission oscillators are parallel, as is the case when the dye is excited in the last absorption band, then[7]

$$\tau_R = 6\tau_F[(1/p_0 - 1/3)/(1/p - 1/p_0)] \quad (2)$$

where τ_F is the fluorescence lifetime and p_0 the degree of polarization measured in an extremely viscous medium. The theoretical upper limit for p_0 is 0.5, and this was indeed observed for I in glycerol. The values obtained in NaLS and methanolic solution are 0.31 and 0.25, respectively. Inserting in eq 2 τ_F(NaLS) = 1.2 and τ_F(MeOH) = 0.24 ns, one calculates τ_R(NaLS) = 1.0×10^{-8} and τ_R(MeOH) = 1.2×10^{-9} s indicating that the rate of rotation is almost one order of magnitude slower in the micellar than in the alcoholic solution. It is concluded that the lifetime of the excited cyanine as well as the fluorescence yield are unequivocally related to the *viscosity* and *not the polarity* present in the local environment of the cyanine dye.

Further studies showed that the nonradiative deactivation of the cyanine S_1 state, which is so effectively blocked in the micellar medium, corresponds in fact to those processes leading to the destruction of the dye. The enhancement of cyanine fluorescence through aqueous micellar systems goes parallel with a remarkable increase of the photostability of the dye. Thus, while irradiation of I in aqueous solution with a 450-W Xe lamp through a 400-nm cut-off filter results in a complete depletion of the dye within 0.5 h, no fading at all could be detected after 24-h irradiation in NaLS micellar solution. Moreover, the micellar cyanine solution is also resistant toward high-intensity laser irradiation. After exposure of such a solution to 50-100 pulses of a 347.1-nm ruby laser (pulse width 20 ns, energy per pulse 250 mJ), no significant alterations of the absorption spectrum could be observed. From the combined effects of fluorescence enhancement and prevention of dye fading exerted by the micellar aggregates, a variety of practical applications may be envisaged. For example, the use of these systems in photographic processes or as dye laser components appears feasible.

The above-described effects have been qualitatively confirmed with a variety of cyanine dyes and merocyanines containing different heterocycles. Surfactants, other than NaLS, $Mg(LS)_2$, and $Cd(LS)_2$, have also been successfully used.

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Models of Siroheme and Sirohydrochlorin. π Cation Radicals of Iron(II) Isobacteriochlorin

Sir:

We here report the preparation of the first synthetic iron complex of the isobacteriochlorin family and demonstrate the existence of π cation radicals of this heme.

The presence of an iron-isobacteriochlorin prosthetic group (siroheme) in two redox enzymes which catalyze the six-electron reductions of sulfite to sulfide (sulfite reductase) and of nitrite to ammonia (nitrite reductase) has recently been elucidated in conjunction with related vitamin B_{12} biosynthetic studies.[2-4] Siroheme has been shown to be the site of interaction between substrate and the electron transport chain, but the mechanism by which siroheme plays this unique role in these multielectron redox enzymes is unknown. Because of the

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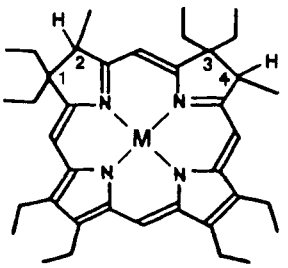
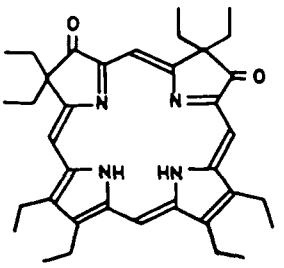
difficulties associated with obtaining the quantities of microbial siroheme needed for extensive studies, the physicochemical properties of this heme and of isobacteriochlorin have to be explored via suitable model compounds. Although tetrahydroporphyrins derived from tetraphenylporphyrin[5] and octaethylporphyrin (OEP)[6] are known, they undergo facile dehydrogenations in the presence of oxidizing material, such as ferric salts, to yield chlorins.[7] We describe here the synthesis of an alkylated isobacteriochlorin which has good stability against dehydrogenation.[8]

Inhoffen and Nolte[9] previously have shown that the reaction of hydrogen peroxide and OEP in acid medium can generate a series of porphyrin ketones in low yields. We have optimized the reaction conditions (82% sulfuric acid at 10 °C using excess H_2O_2) such that the overall yield of porphyrin diketones exceeds 20%.[10,11] The *gemini*-diketoporphyrin **2** was isolated by



1a M = 2H
1b M = Fe



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chromatography on a silica gel column using methylene chloride–hexane mixtures as eluant. Conversion of the diketoporphyrin to the methylated isobacteriochlorin was achieved by reacting **2** with methyllithium, followed by hydrolysis; the resultant tertiary alcohols were then reduced with HI–H_3PO_2–AC_2O.[11] 2,4-Dimethyl-*gemini*-octaethylisobacteriochlorin (**1a**, DMOEiBC) thus obtained consisted of diasteric isomers which could not be separated by LC. NMR (180 MHz, $CDCl_3$) showed the meso protons at 8.35, 7.28, 7.13, and 6.56 ppm, in close agreement with those of sirohydrochlorin,[2] the demetalated siroheme which is also a vitamin B_{12} biosynthetic precursor. The inner nitrogen protons were found at δ 3.6, vs. the ~2–3 observed in sirohydrochlorin and octaethylisobacteriochlorin.[2] Reaction of **1a** and ferrous perchlorate in pyridine–acetic acid under argon afforded the violet pyridine hemochrome in almost quantitative yield (monitored by quenching of the intense orange fluorescence of the free base). The ferric complex can be isolated by washing with dilute aqueous HCl; further purification by chromatography on alumina is usually not required. The ferrous heme in pyridine readily reacted with CO to give a grayish-green-colored CO complex with an absorption spectrum nearly identical with that of its siroheme counterpart[12,13] (Figure 1).

The redox chemistry of **1a** and its metal derivatives have been examined using cyclic voltammetry and controlled potential coulometry. The redox potentials of DMOEiBC and of the corresponding chlorins and porphyrins are listed in Table I. Notable features of these results are that the redox potentials of hydroporphyrins are invariably displaced to more negative values; i.e., they are easier to oxidize but harder to reduce. Nonetheless, except for tetrabenzporphyrin (TBP), the separation between the 1st ring oxidation and reduction potentials, which reflects the HOMO and LUMO energy gap,[14] remains relatively constant throughout the porphyrin–chlorin–isobacteriochlorin series. This suggests that saturation of the pyrrole double bonds exerts its effect mainly by σ donation on the ring, whereas the conjugated benzene rings in TBP perturb the π cloud more effectively.

As a result of the extremely low oxidation potential of the isobacteriochlorin skeleton, it becomes possible for **1b** to *lose an electron from the ring rather than from the central metal ion.* As shown in Figure 2, one-electron oxidation of Fe^{II}-

Table I. Redox Potentials of Isobacteriochlorin and Porphyrin Derivatives (vs. SCE)[a]

compd	$E_{1/2}$[b]	$E_{1/2}^{ring \rightarrow ring^+\cdot}$	$E_{1/2}^{Fe^{III} \rightarrow Fe^{II}}$	$E_{1/2}^{ring \rightarrow ring^-\cdot}$
DMOEiBC				
free base		0.37		−1.72
Zn		0.08		−1.95
$Fe^{III}Cl$	0.44		−0.4[c]	
$Fe(Py)_2$			−0.04	
Fe(Py)(CO)		0.13		
Fe(1-MeIm)$_2$			−0.34	
Fe(1-MeIm)(CO)		0.05		
Etiochlorin I[d]				
free base		0.63		−1.45
Zn		0.36		−1.60
$Fe^{III}Cl$	0.68		−0.4[c]	
$Fe(Py)_2$			−0.04	
Fe(Py)(CO)			0.35[i]	
OEP				
free base[e]		0.83		−1.45
Zn[e]		0.63		−1.61
$Fe^{III}Cl$	0.94		−0.5[c]	
$Fe(Py)_2$			−0.02	
Fe(Py)(CO)			0.52[i]	
TBP[f]				
Free base–Me_2SO		0.55[g]		−1.13
Zn–Me_2SO		0.38[h]		−1.46[h]
$Fe(py)_2$			0.23	
Fe(Py)(CO)		0.47		

[a] Oxidations in CH_2Cl_2, reductions in butyronitrile (TBP and ZnTBP in Me_2SO) with 0.1 M tetra-*n*-butylammonium perchlorate. Pyridine complexes were run in CH_2Cl_2 containing 20% pyridine and imidazole complexes in 20% 1-methylimidazole in CH_2Cl_2. [b] Ring oxidation or $Fe^{III} \rightarrow Fe^{IV}$; see text. [c] Quasi-reversible. [d] Prepared according to W. Schlesinger, A. H. Corwin, and L. J. Sargent, *J. Am. Chem. Soc.*, **72**, 2867 (1950). [e] See ref 18. [f] Prepared according to A. Vogler and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, **17**, 760 (1978). [g] Poor solubility; waves were not well defined. [h] A. Vogler, B. Rethwisch, H. Kunkely, J. Hüttermann, and J. O. Besenhard, *Angew. Chem., Int. Ed. Engl.*, **17**, 951 (1978), reported 0.36 and −1.48 V, respectively. [i] Irreversible.

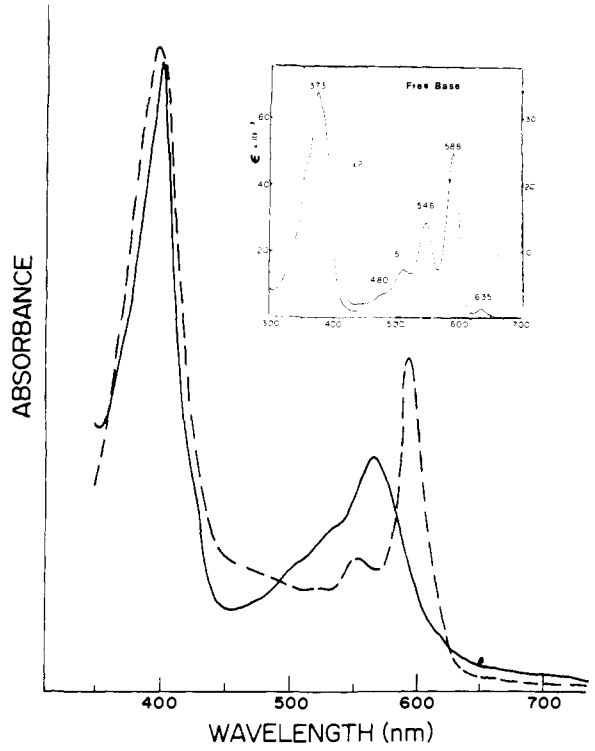

Figure 1. Absorption spectra of **1b** in pyridine (—) and of the CO complex of **1b** in pyridine (- - -). The heme was reduced by a trace amount of 95% hydrazine. Inset: **1a** in CH_2Cl_2.

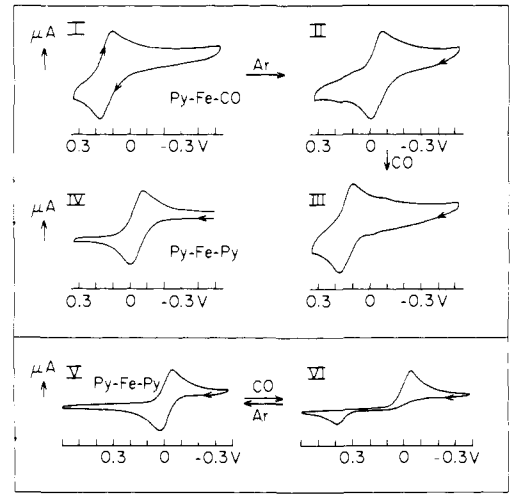

Figure 2. Cyclic voltammograms of iron DMOEiBC (I-IV) and iron etiochlorin I (V-VI), performed in CH_2Cl_2 containing 20% pyridine by volume with 0.1 M tetra-*n*-butylammonium perchlorate. Scan rate: 200 mV/s. I: **1b** was reduced by hydrazine hydrate in a CO-saturated solution of CH_2Cl_2-pyridine-water (4:1:5). The organic layer was withdrawn with a gas-tight syringe and 50 μL of this solution was added to the CV apparatus which contained CO-saturated CH_2Cl_2-pyridine. The final concentration of the heme was $\sim 10^{-4}$ M. II: after passing argon gas in I for 5 min. III: after passing CO in II for 3 min. IV: **1b** dissolved in CH_2Cl_2-pyridine, under argon. V: ferric (or ferrous) etiochlorin dissolved in CH_2Cl_2-pyridine, under argon. VI: after passing CO in V for 3 min. During the oxidation scan (toward left), CO-heme was oxidized to Fe(III) species which could no longer bind CO and was not reduced until the potential swept across the pyridine hemochrome reduction region (−0.05 V). Once reduced, the ferrous heme complexed with CO instantaneously and the CO-heme could not be oxidized at the pyridine hemochrome oxidation potential.

(DMOEiBC)(Py)(CO) yields a π cation radical which still binds CO, $Fe^{II}(DMOEiBC)^{+}\cdot(Py)(CO)$. On the other hand, oxidation of a corresponding iron porphyrin or chlorin yields only an Fe(III) species which does not bind CO. Tetrabenzporphyrin derivatives, however, can also lose an electron easily from the ring because of the low oxidation potential, and an $Fe^{II}(TBP)^{+}\cdot(Py)(CO)$ radical has indeed been reported recently.[15] From our own study of $Fe^{II}(TBP)(Py)(CO)$, reversible waves similar to those shown in Figure 2 (I-III) have been obtained. $Fe^{II}(DMOEiBC)(Py)(CO)$ in methylene chloride exhibits an IR absorption at 1970 cm^{-1}, while the oxidized cation radical has a ν_{CO} of 2010 cm^{-1}. This 40-cm^{-1} shift corresponds well with the 45-cm^{-1} shift observed in the TBP system[15] and reflects the decreased overall electron density in the ring oxidized heme.[16]

The assignment of the ring oxidation is further supported by EPR evidence. $Fe^{II}(DMOEiBC)^{+}\cdot(Py)(CO)$ generated by I_2 oxidation exhibited an EPR signal at room temperature in CH_2Cl_2, with a g value of 2.003 and a partially resolved three-line spectrum (Figure 3). This spectrum is very similar to those observed for $H_2DMOEiBC^{+}\cdot$ and $ZnDMOEiBC^{+}\cdot$ which have been assigned to interaction with the two protons on the saturated pyrrole rings.[17] This signal quickly disappeared when the sample was purged with an inert gas. (Paramagnetic iron(III) cannot be detected under these experimental conditions.) The radical species exhibits a broad, featureless absorption spectrum in the visible region with a Soret band centered at ~385 nm. Both the optical and EPR spectra are consonant with those of π cation radicals of other metalloisobacteriochlorins.[18]

The redox properties of $Fe^{III}(DMOEiBC)Cl$ are also noteworthy (Table I). While Fe(III)-π cation radicals of porphyrins appear to be ruled out in favor of an Fe(IV) state,[19,20] the reversible, one-electron half-wave at +0.44 V of Fe^{III}(**1a**)Cl suggests that, in isobacteriochlorins, the ring rather than the iron, would undergo oxidation.[21] This notion is certainly reinforced by the Fe(II) radical evidence presented

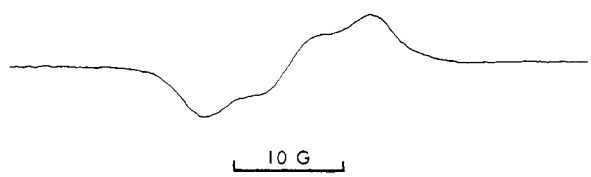

Figure 3. ESR spectrum of $[Fe^{II}(DMOEiBC)(Py)(CO)]^{+}\cdot$ in CH_2Cl_2 at 20 °C. Oxidation was by I_2.

above. Furthermore, even in porphyrins, π cation radicals are considered to mediate electron transfer in the enzymatic cycles of catalase and horse radish peroxidase.[22-24] Our model studies reported here raise the possibility that similar electron pathways involving the π system may obtain in the biological function of siroheme and that the facile oxidations of the isobacteriochlorins dictate the choice of that macrocycle in sulfite and nitrite reductases.

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Carbon–Carbon Cleavage during Birch–Hückel-Type Reductions[1]

Sir:

Recently it was reported[2] that the action on coal (Westerholt Mine, Robert Seam, 24% volatile) of potassium in a mixture of glyme and triglyme, followed by quenching with water, (a) reduced the coal in three passes from $C_{100}H_{63}O_{3.2}$ to fractions of composition $C_{100}H_{144}O_{1.8}$ (soluble) and $C_{100}H_{91}O_{3.4}$ (insoluble) and (b) diminished the molecular weight of the soluble sample from $>10^5$ to values of 3000–5000. It further appeared, from spectral (NMR and quantitative IR) data, that the methyl-group content of the product increased with increased hydrogen uptake; i.e., ~40% of the hydrogen uptake was related to the increase in methyl-group content. This is a surprising conclusion, for it implies the cleavage of *aliphatic* carbon–carbon bonds in the coal structures and is contrary to the commonly held concept of the Birch–Hückel reduction,[3,4] in which aromatic rings are reduced to cycloalkenes.

Not only protic solvents, but also ethers[4] and alkyl halides, may be used[5,6] as quenchers, with the formation, e.g., from naphthalene, of methyl-[5] and isopropylnaphthalenes.[6] A less drastic reduction prior to the alkylation procedure has been applied to coal by Sternberg and co-workers.[7] However, this reduction method may be seen as being related to the Birch–Hückel reduction. Sternberg and co-workers explained the high solubility of the product by (a) cleavage of ether linkages to form phenolate anions, (b) C-alkylation of the aromatic anions, and (c) O-alkylation of the phenolate anions. A similar reduction procedure by direct insertion of potassium has been reported,[8] and the formation of the potassium graphite intercalation compound by treating graphite with potassium naphthalene[9] links these unconventional reduction methods to the more common Birch–Hückel method.

There is some evidence for cleavage of aliphatic carbons during Birch–Hückel reductions in highly substituted, hindered compounds,[3b,10-12] and Langendijk and Swarc[13] reported spectral evidence for cleavage of 1,2-di(α-napthyl)ethane by sodium in THF, THP, DME, and HMPA.[14] However, other authors[12c,15] found that 1,2-diphenylethane cannot be cleaved in ether. (In unpublished work,[16] Grovenstein and co-workers have found that cesium–sodium–potassium alloy will cleave bibenzyl and several of its derivatives.)

For the reasons mentioned above we studied the reactions of sodium–potassium alloy in the solvent system glyme–triglyme[2] on a series of model compounds to determine whether, in fact, the Birch–Hückel reduction can be used in this solvent system to cleave carbon–carbon bonds. In the first series of experiments—to simplify product analysis—methyl-^{14}C iodide[17] was used to quench the solutions. The reactions were all carried out at the same temperature (0 °C) and concentrations and for the same lengths of time (3 h).[18] Conditions were not optimized. Since the products were analyzed by GC,[18] the yields are reported as percent composition of the components which pass through the chromatograph. The reactants, products, and yields[18] are shown (reactions 1–5). *meso*- and *dl*-

$PhCH_2CH_2Ph$ (100% reaction)

$$\xrightarrow[2.\ {}^*CH_3I]{1.\ NaK} PhCH_3\ (37\%) + PhCH_2\overset{+}{C}H_3\ (42\%) + PhCH(\overset{*}{C}H_3)CH_2Ph\ (21\%) \quad (1)$$

$PhCH(CH_3)CH_2Ph$ (83%)

$$\xrightarrow[2.\ {}^*CH_3I]{1.\ NaK} PhCH_3\ (13\%) + PhCH_2\overset{*}{C}H_3\ (22\%)$$

$$+ PhCH(CH_3)_2\ (23\%) + PhCH(CH_3)-CH(CH_3)Ph\ (24\%\ meso,\ 18\%\ dl) \quad (2)$$

$PhCH_2Ph$ (88%)

$$\xrightarrow[2.\ {}^*CH_3I]{1.\ NaK} PhCH_3\ (12.5\%) + PhCH(\overset{*}{C}H_3)Ph\ (54.5\%) + PhC_6H_4CH_2Ph\ (33\%\ ortho,\ meta,\ para) \quad (3)$$

$CH_3C_6H_4CH_2Ph$ (67%)

$$\xrightarrow[2.\ {}^*CH_3I]{1.\ NaK} CH_3C_6H_4CH(\overset{*}{C}H_3)Ph\ (64\%) + PhC_6H_4CH_2C_6H_4CH_3\ (25\%\ ortho,\ meta,\ para) \quad (4)$$

$PhCH(CH_3)Ph$ (44%)

$$\xrightarrow[2.\ {}^*CH_3I]{1.\ NaK} PhCH_2CH_3\ (41\%) + PhC(\overset{*}{C}H_3)Ph\ (59\%) \quad (5)$$

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