Synthesis of Zn-, Mn-, and Fe-Containing Mono- and Heterometallated Ethanediyl-Bridged Porphyrin Dimers

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New ethanediyl-bridged unsymmetrical mono- and heterometallated dimers of 2,3,7,8,12,13,17,18-octa-ethyl-21H,23H-porphyrin (H$_2$oep) containing transition-metal ions (Mn and Fe) were synthesized by a facile stepwise metallation/demetallation process under mild conditions. The novel metallation strategy initially involved the predominant insertion of Zn into one of the two porphyrin rings of the free-base dimer, followed by the incorporation of Mn or Fe into the other porphyrin ring under exceptionally mild conditions, giving corresponding heterometallic dimers; the subsequent removal of Zn yielded mono-transition-metal dimers. The emission spectrum of the monozinc dimer predominantly exhibited fluorescence bands of the free-base porphyrin component, indicating a very efficient energy-transfer process. Conversely, emission of the free-base or Zn porphyrin component of transition metal containing dimers was strongly quenched due to photoinduced electron transfer.

1. Introduction. – To date, covalently linked mono- and heterometallated porphyrin dimers or oligomers have attracted much attention as efficient photosynthetic models of electron transfer [1], singlet or triplet energy transfer [2], interchromophore interactions [3], catalytic systems [4], potential microelectronic molecular devices [5], and tumor-localizing diagnostic agents [6].

There are two general synthetic strategies for the preparation of mono- and heterometallated covalently linked porphyrin systems (*Scheme 1*). The first approach involves the coupling of two or more appropriately modified porphyrin monomers with different inserted central metal ions and/or porphyrin free bases, or the stepwise construction of heterodimeric structure from a suitably derivatized monoporphyrin [2a,c–e,g,m] [6] [7] (*Scheme 1,a*). The second approach is based on the initial construction of a dimeric or oligomeric structure consisting of porphyrin rings (*e.g.* bis-(free-base) or bis-homometallic complexes). This is followed by the metallation or demetallation of one macrocycle to yield the monometallated porphyrin dimer or oligomer, and then a different metal ion is inserted to produce a heterometallic system [1b] [2] [3a,d,e] [8] (*Scheme 1,b*). Additionally, the possibility of a highly selective metal insertion into dimeric or oligomeric porphyrin structures in which modifications protect one porphyrin ring through artificially constructed steric hindrances is also noteworthy, such as in the case of 'doubly strapped' porphyrin units [9].

All of these strategies have inherent advantages and disadvantages, and the choice is dependent mostly on the target structures. Whereas the first method may lead directly to the desired heterodimeric or oligomeric porphyrins, there are limitations on the stability and solubility of some monomeric metalloporphyrins towards the necessary coupling conditions. For example, [Zn(porphyrinato)] complexes, which are used frequently as effective photoexcited electron- or energy-donor components in

Scheme 1
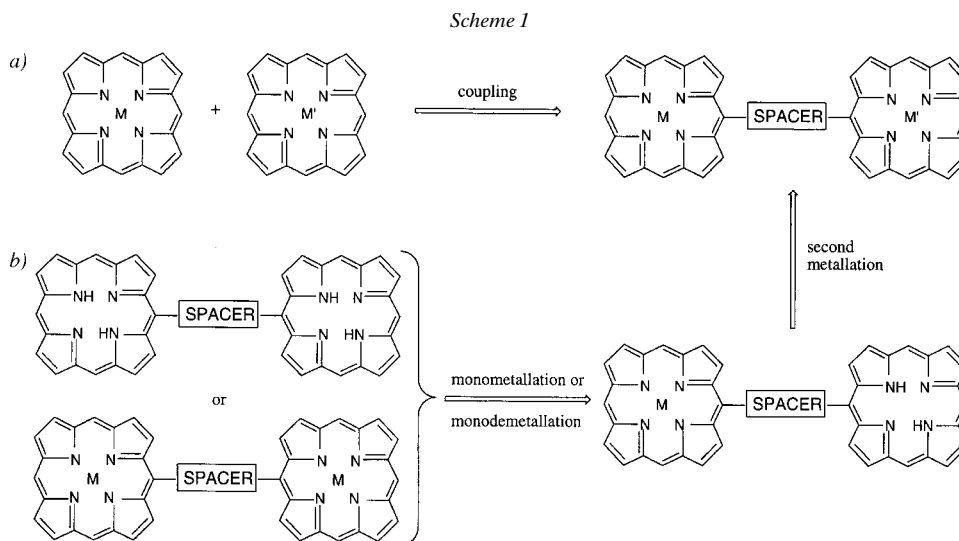
supramolecular multicomponent systems [10], are relatively unstable, even under weakly acidic conditions. The mixture of porphyrin dimers or oligomers formed during the coupling of the different monomers bearing the same reactive group also presents its own problems.

The second approach gives more synthetic flexibility, allowing the production of a greater diversity of monometallic and heterometallic systems from the same initial porphyrin dimers or oligomers. However, the shortcomings of this method include a low selectivity for the monometallation or monodemetallations and a possible transmetallation process during the second metallation. Furthermore, the conventional methods [11] for incorporating transition-metal ions (Fe and Mn) which are frequently applied in the preparation of strong electron acceptors [1a–e,l,m] or catalytic sites for oxygen binding and oxidation reactions [4][12] require the use of severe conditions (*e.g.* refluxing DMF or AcOH) which can lead to decomposition of the dimeric or oligomeric structures.

We now describe a novel, simple, and convenient synthesis [13] of heterometallic porphyrin dimers **1–4** containing a photosensitizer (free-base porphyrin or [Zn(por-phyrinato)] moiety) and an electron acceptor ([Fe(porphyrinato)] or [Mn(porphyr-
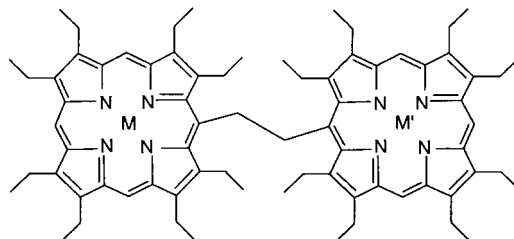
1 M = Zn, M' = $Mn^{3+}Cl^-$ **3** M = 2H, M' = $Mn^{3+}Cl^-$
2 M = Zn, M' = $Fe^{3+}Cl^-$ **4** M = 2H, M' = $Fe^{3+}Cl^-$

inato)] moiety) covalently linked *via* an ethanediyl bridge. Since our target structures consist of the same ethanediyl-linked porphyrin moieties with different metal ions inserted, and since some dimers (**1** and **2**) contain an unstable Zn ion, the second synthetic approach outlined above is the best suited for their preparation.

2. Results and Discussion. – 2.1. *Preamble*. The general synthetic strategy includes the selective Zn-ion incorporation into one of the linked porphyrin rings followed by Mn or Fe insertion into the other porphyrin moiety to give heterometallic dimers **1** and **2** by a recently modified method [13][14] for transition metal ion insertion under mild conditions. To obtain monometallated dimers **3** and **4**, the Zn ion was selectively removed by weak acidic treatment.

2.2. *Free-Base Dimer* **10**. The free-base dimer **10** was synthesized according to *Scheme 2* by applying recently modified coupling methods [15][16] to the established procedure [8d,e]. The Cu complex **6**, obtained quantitatively by treatment of free base **5** with $Cu(OAc)_2$, was reacted with the *Vilsmeier* complex formed by mixing $POCl_3$ and DMF, giving the corresponding *Vilsmeier* salt **7**. The progress of the reaction was easily followed by TLC. The intermediary iminium salt **7** was reduced with $NaBH_4$ in $CHCl_3/MeOH$ to give the key monomer **8** (88% yield) for the subsequent self-coupling reaction. Dimerization of **8** was carried out in refluxing MeI/CH_2Cl_2 [15][16] (TLC monitoring). After chromatographic purification, the yield of **9** was 67%. Demetallation of **9** with conc. H_2SO_4 solution gave the corresponding free-base dimer **10** in nearly quantitative yield. Only traces (*ca*. 1%) of the partially demetallated heterodimer **11** were observed, and this could be further demetallated by repeating this process.

2.3. *Intermediate Monometallated Dimer* **12**. The Zn ion was chosen as the first metal to be inserted into one of the porphyrin rings of the free-base dimer **10** (*Scheme 3*). This strategy allowed frequent TLC monitoring and easy chromatographic separation of the reaction mixture **10/12/13** since the R_f values (silica gel, $CHCl_3$) were easily distinguishable. Additionally, the use of mild conditions for Zn demetallation permitted a fast and complete separation of **10** from the dizinc dimer **13**, which was formed as an unavoidable by-product during the Zn-ion incorporation. A recently reported method [3a] for partial incorporation of Zn ion into **10** gave mono- and dizinc complexes **12** and **13** in 49% and 22% yield, respectively. To achieve a more selective monometallation, we modified this procedure and adopted a dropwise addition of 1.2 equiv. of $Zn(OAc)_2$ in MeOH to a refluxing CH_2Cl_2 solution of **10**. Frequent TLC monitoring allowed us to establish optimized conditions for a maximum yield of the monometallated dimer **12**. Chromatographic separation (silica gel, $CHCl_3$) of the resultant mixture gave pure **12** and **13** in 60% and 22% yield, respectively. Treatment of the dizinc dimer **13** with 6M HCl regenerated the starting material **10** quantitatively.

2.4. *Effective New Synthetic Method for Fe- and Mn-Ion Insertion into Porphyrins*. Initial attempts to insert a Mn ion into the free-base porphyrin ring of heterodimer **12** by *Adler*'s conventional procedure [11] with $MnCl_2$ in refluxing DMF failed completely, giving a complex mixture of several Mn complexes and unidentified products, probably due to thermal decomposition of the dimeric structure and/or transmetallation. Since the resulting Mn complexes had similar R_f values on TLC, analysis and efficient chromatographic separation seemed to be a very difficult task. Several unsuccessful attempts prompted us to develop a novel, more selective and efficient
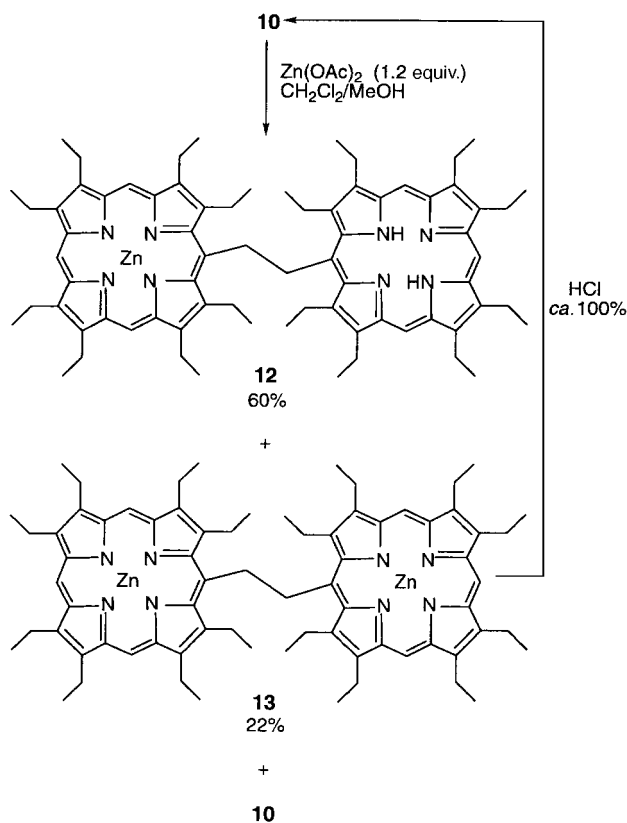
Scheme 2
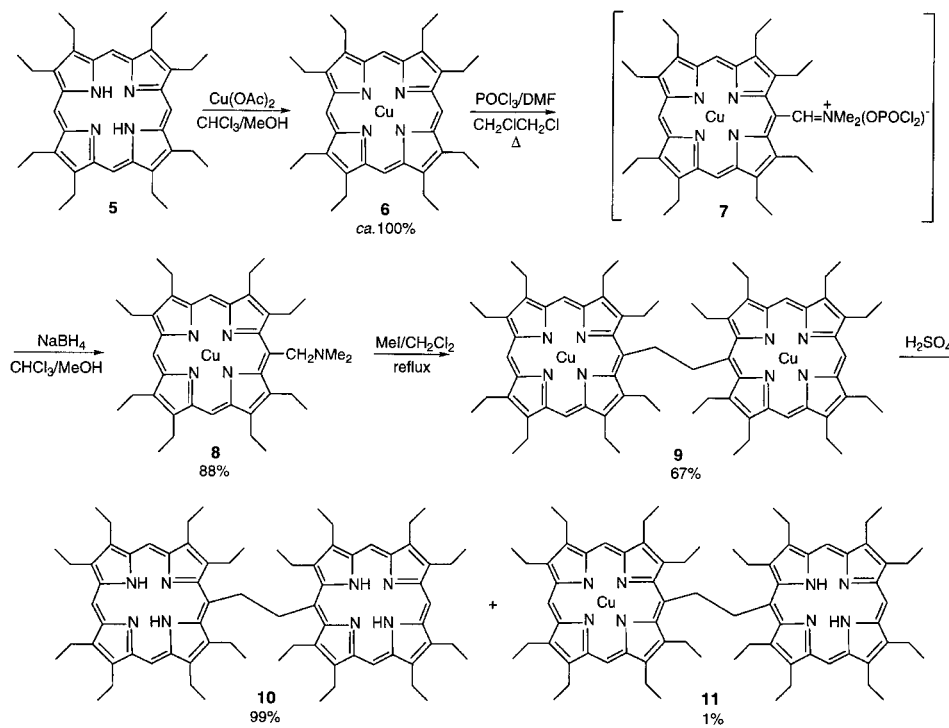
method [14] for insertion of transition-metal ions into the porphyrin ring under mild conditions.

The reaction conditions of the new procedure, shown in *Scheme 4*, were optimized for the metallation of 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin (H$_2$oep). The course of the reaction was followed by TLC, with commercially available [Mn(oep)] as the reference. At first, it was found that addition of 16 equiv. of MnCl$_2$ in MeOH to H$_2$oep in CHCl$_3$, followed by stirring for 24 h at room temperature led to [Mn(oep)] in a maximum yield of 50%. However, the subsequent addition of a few drops of 2,6-lutidine (= 2,6-dimethylpyridine) shifted the equilibrium towards the desired product, and the quantitative formation of [Mn(oep)] was observed after 5 h. Control experiments also revealed that no transmetallation of [Zn(oep)] occurred.
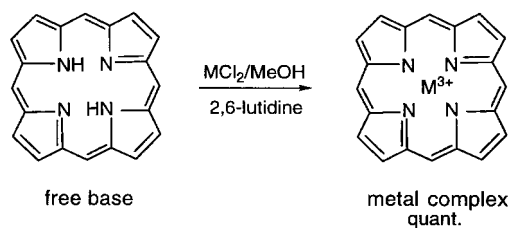
The conditions were also successfully applied to Fe-ion insertion into H$_2$oep. It is significant that the rate of Fe-ion insertion was much faster than that of Mn insertion. Thus, the quantitative conversion of H$_2$oep to [Fe(oep)] was completed within 1 h at room temperature, whereas under the same conditions, [Zn(oep)] suffered some transmetallation reaction to form [Fe(oep)] in *ca.* 10% yield, due to the higher reactivity of FeCl$_2$.

This metal-insertion procedure was tested on a variety of lipophilic and hydrophilic, non-tetraphenyl- and tetraphenyl-type monomeric porphyrins (*Table 1*) [14]. To the best of our knowledge, these metal-incorporation conditions are the mildest and most effective among reported methods [11][16], yet require only homogeneous reaction

Scheme 3

10

Zn(OAc)$_2$ (1.2 equiv.)
CH$_2$Cl$_2$/MeOH

HCl
*ca.*100%

12
60%

+

13
22%

+

10

Scheme 4

MCl$_2$/MeOH

2,6-lutidine

free base   metal complex
quant.

media, room temperature (or slight heating), and short to moderate reaction times, but no inert atmosphere or high-purity solvent. The apparent advantages of this method include its general applicability to different porphyrin structures, especially those which are thermally unstable, offering high yields and quantitative conversions which lead to easy workup procedures and product separation.

2.5. *Hetero- and Monometallated Dimers* **1** – **4**. The above-described method for Mn- and Fe-ion insertion was applied to the second metallation of **12** to produce the target heterometallic dimers **1** and **2** (*Scheme 5*). This new and efficient method was

Table 1. *Reaction Conditions for the Transition-Metal Insertion into Different Porphyrins*

Porphyrin[a]	Metal salt	Reaction conditions[a]
H_2oep	$MnCl_2$	$CHCl_3$/MeOH/L, r.t., 5 h[b]
	$FeCl_2$	$CHCl_3$/MeOH/L, r.t., 1 h[b]
H_2cptme	$MnCl_2$	$CHCl_3$/MeOH/L, r.t., 7 h[b]
	$FeCl_2$	$CHCl_3$/MeOH/L, r.t., 3 h[b]
H_2cp	$MnCl_2$	MeOH/L, r.t., 20 h[b]
	$FeCl_2$	MeOH/L, r.t., 7 h[b]
H_2mp	$MnCl_2$	MeOH/L, r.t., 20 h[b]
	$FeCl_2$	MeOH/L, r.t., 7 h[b]
H_2ttp	$MnCl_2$	$CHCl_3$/MeOH/L, r.t., 8 h[b]
	$FeCl_2$	$CHCl_3$/MeOH/L, 40°C, 1 h[b]
		$CHCl_3$/MeOH/L, 35°C, 3 h[b]
H_2tmpyp	$MnCl_2$	H_2O/MeOH/L, r.t., 24 h[b]

[a]) Abbreviations: octaethylporphyrin (H_2oep), coproporphyrin I tetramethyl ester (H_2cptme), coproporphyrin I (H_2cp), mesoporphyrin IX (H_2mp), tetraphenylporphyrin (H_2tpp), tetramethylpyridylporphyrin (H_2tmpyp), 2,6-lutidine (L). [b]) Full conversion.

most advantageously used in the Mn-ion incorporation into the free-base ring of monometallated dimer **12** to give the heterodimer **1** quantitatively. The same procedure employed for the introduction of Fe ion into **12** resulted in moderate success, affording the heterodimer **2** in 46% yield. The higher reactivity of a ferrous salt (*Table 1*) under these conditions probably accelerated the unwanted transmetallation reaction, producing homodimer **14** in 25% yield as a by-product.

Scheme 5
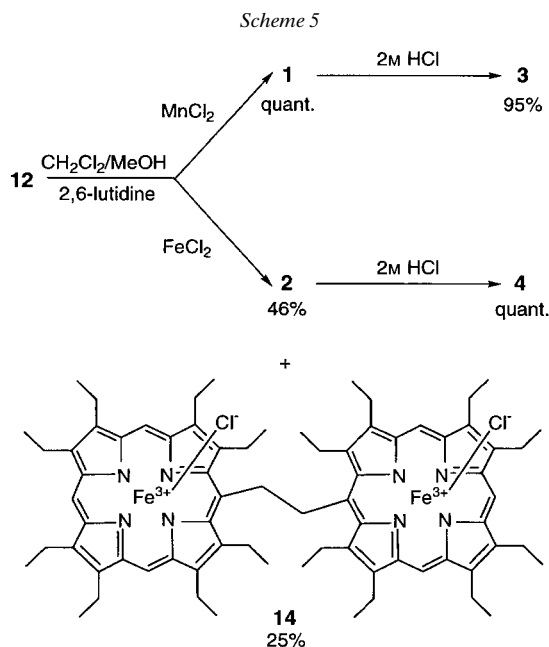
Attempts to optimize the Fe-ion insertion procedure by lowering the reaction temperature to avoid a transmetallation side reaction resulted in moderate success. Thus, the Fe-ion incorporation into H_2oep at 0° proceeded slowly and produced just 10–15% of [Fe(oep)] after 3 h and *ca.* 60–65% of [Fe(oep)] after 28 h, whereas no transmetallation of [Zn(oep)] was observed at this temperature. However, Fe metallation of monozinc dimer **12** under these conditions showed less than 20% conversion of the initial dimer **12** after 24 h. Gradual warming to r.t. and workup followed by repeated chromatographic separation gave a mixture of the target heterodimer **2** and by-product **14**, in 36 and 17% yield, respectively.

Finally, in order to selectively remove the Zn ion from one porphyrin ring of the heterometallic dimers **1** and **2** without Fe- or Mn-ion demetallation from the second porphyrin ring, several trial reactions were carried out. Thus, treatment of [Zn(oep)] with 4M and 2M HCl led to a fast and complete demetallation to give H_2oep, while after 1M HCl treatment, some [Zn(oep)] remained. At the same time, an examination of [Fe(oep)] and [Mn(oep)] stability toward acidic conditions revealed that 4M HCl treatment of [Fe(oep)] resulted in some amount of fluorescent demetallated product (apparently H_2oep), whereas 2M HCl treatment of [Mn(oep)] showed no detectable demetallation (it is commonly understood that [Fe(porphyrinato)] complexes are generally more stable in acidic media than Mn complexes). Based on these observations, 2M HCl treatment was applied for selective Zn-ion demetallation of the heterometallic dimers **1** and **2** to give the corresponding monometallated dimers **3** and **4** in quantitative yield (*Scheme 5*).

The dimers were characterized by FAB mass spectrometry (for **1**–**4**, **10**, and **12**–**14**) and ¹H-NMR (for **10**, **12**, and **13**), UV/VIS (for **1**–**4**, **10**, and **12**–**14**), and fluorescence spectroscopy (for **1**–**4**, **10**, **12**, and **13**). The purity of all the compounds was also confirmed by TLC (silica gel).

2.6. *Mass Spectra.* The observed profiles of FAB mass spectra of the dimers **1**–**4**, **10**, **12**–**14** are consistent with the calculated isotope patterns and clearly exhibit peaks corresponding to the molecular ion (M^+), as well as fragment peaks due to a homolytic fission of the ethanediyl bridge. An interesting feature observed in the spectrum of diiron dimer **14** is an intense peak at m/z 1355 ($[M+152]^+$) which is attributed to a 1:1 complex of **14** with 3-nitrobenzyl alcohol (NBA), which was used as a matrix for MS measurements.

2.7. *¹H-NMR Spectra.* High-resolution ¹H-NMR spectra of the target dimers **1**–**4** are not available due to the presence of paramagnetic Mn or Fe ions in one of the porphyrin rings. ¹H-NMR Spectra of the initial and intermediate dimers **10**, **12**, and **13** reflect their structural organization and coincide with ¹H-NMR spectra reported previously [3a][8e][17]. Recently, it was concluded [3a][17] that only Zn ion containing ethanediyl-bridged dimers adopt a '*syn*' conformation in nonpolar solvents due to attractive π-π interaction between the porphyrin macrocycles. It is noteworthy that our ¹H-NMR data also support this assumption, establishing a predominant '*syn*' conformation in the case of **12** and **13**.

Thus, the chemical shifts of the *meso*-protons H−C(10) and H−C(20) of the zinc-containing dimers **12** and **13** and of the pyrrole NH of monometallated dimer **12** are shifted considerably upfield ($\Delta\delta = 0.98$–1.05 ppm and 1.61 ppm for *meso*-H of **12** and **13**, resp., and 1.5–1.85 ppm for NH of (**12**) in CDCl₃ at room temperature. The $\delta(H)$ of the ethanediyl bridge have a small downfield shift ($\Delta\delta = -0.31$ ppm for one CH₂ group of **12** and

− 0.19 for **13**) in comparison with those of the corresponding protons of **10**. The shielding of the *meso*-protons and pyrrole NH is due to the ring-current effect of the neighboring porphyrin cycle, and the deshielding of the ethanediyl protons is a result of the CH_2 group lying outside the induced magnetic field of the porphyrin moieties. These changes are typical of porphyrin dimers in the fixed 'face-to-face' spatial orientation [18] and clearly indicate a predominance of '*syn*' conformation for **12** and **13**. Furthermore, the side-chain MeCH_2 protons of **12** and **13** were observed as eight nonequivalent signals (δ 4.32 – 2.40) which is very similar to the corresponding signals of *cis*-ethylenediyl-bridged dimers [17][18a].

2.8. *Absorption Spectra*. UV/VIS spectra of heterodimers **1** – **4** in CHCl$_3$ (*Fig. 1,a* and *b*) are comprised of the absorptions of the individual porphyrin moieties. Thus, the Mn ion containing dimers **1** and **3** share the intense absorption of [Mn(porphyrinato)] at *ca*. 485 nm in the Q-band region, in addition to their own characteristic bands which belong to the Zn and free-base porphyrins. The *Soret* bands of **1** – **4**, all of which are found in the same region (*ca*. 414 – 418 nm), do not show an appreciable deviation from the original position observed for **10**. According to the exciton-coupling theory [19], these red-shifted *Soret* bands, often observed for the linearly linked porphyrin dimers [20][3a,d][8b,c,e][17][20] and porphyrin *J*-aggregates [21], indicate the predominant formation of a 'head-to-tail' B-transition orientation.

In sharp contrast to the spectra of heterodimers **1** – **4**, the *Soret* bands of the dizinc complex **13** and monozinc dimer **12** are blue-shifted (*Fig. 1,c*), with the maxima appearing at 398 and 406 nm, respectively. At the same time, the Q-bands attributable to the [Zn(porphyrinato)] component of these dimers are slightly red-shifted. These spectral changes were also observed recently for ethanediyl-bridged zinc dimers [3a][17], and are caused by exciton interactions between porphyrin chromophores brought together into cofacial proximity, as is the case for covalently linked porphyrin dimers in coplanar conformation [3c,e][4a][18a – f] and porphyrin H-aggregates [21a,c,e – g].

These observations are in agreement with the ^{1}H-NMR data and clearly indicate that the dimers **12** and **13** adopt mostly the '*syn*' conformation, while the heterodimers **1** – **4** are in '*anti*' conformation. However, a twofold broadening and smaller red shift of the *Soret* band of monozinc dimer **12** in comparison with dizinc dimer **13** may be the result of an appreciable contribution of the corresponding '*anti*' conformer in solution (for the detailed conformational study, see [22]).

2.9. *Fluorescence Spectra*. In general, paramagnetic metalloporphyrins possess very short-lived excited electronic states and do not exhibit any appreciable emission. This is due to the existence and possible mixing of different excited states of porphyrin ligand ($\pi\pi^*$) and metal ion (dd or ff) and/or ligand-metal charge-transfer states (πd*/πf* or dπ*/fπ*) which may produce strong vibronic and spin-orbital couplings between the states. This may result in the fast and radiationless deactivation of the excited states, or the acceleration of intersystem crossing to the triplet state. Therefore, only the fluorescence of the free base or [Zn(porphyrinato)] moieties could be detected in the emission spectra of the mixed dimers **1** – **4**.

In the emission spectra (*Fig. 2,a* and *c*), the fluorescence intensities of heterodimers **1** – **4** are dramatically reduced in comparison with those of the corresponding dizinc dimer **13** or free-base dimer **10** (*Table 2*). This fluorescence quenching can be attributed to an intramolecular electron transfer from the singlet excited state (S$_1$) of the Zn or free-base porphyrin chromophore to the [Mn^{III}(porphyrinato)] or
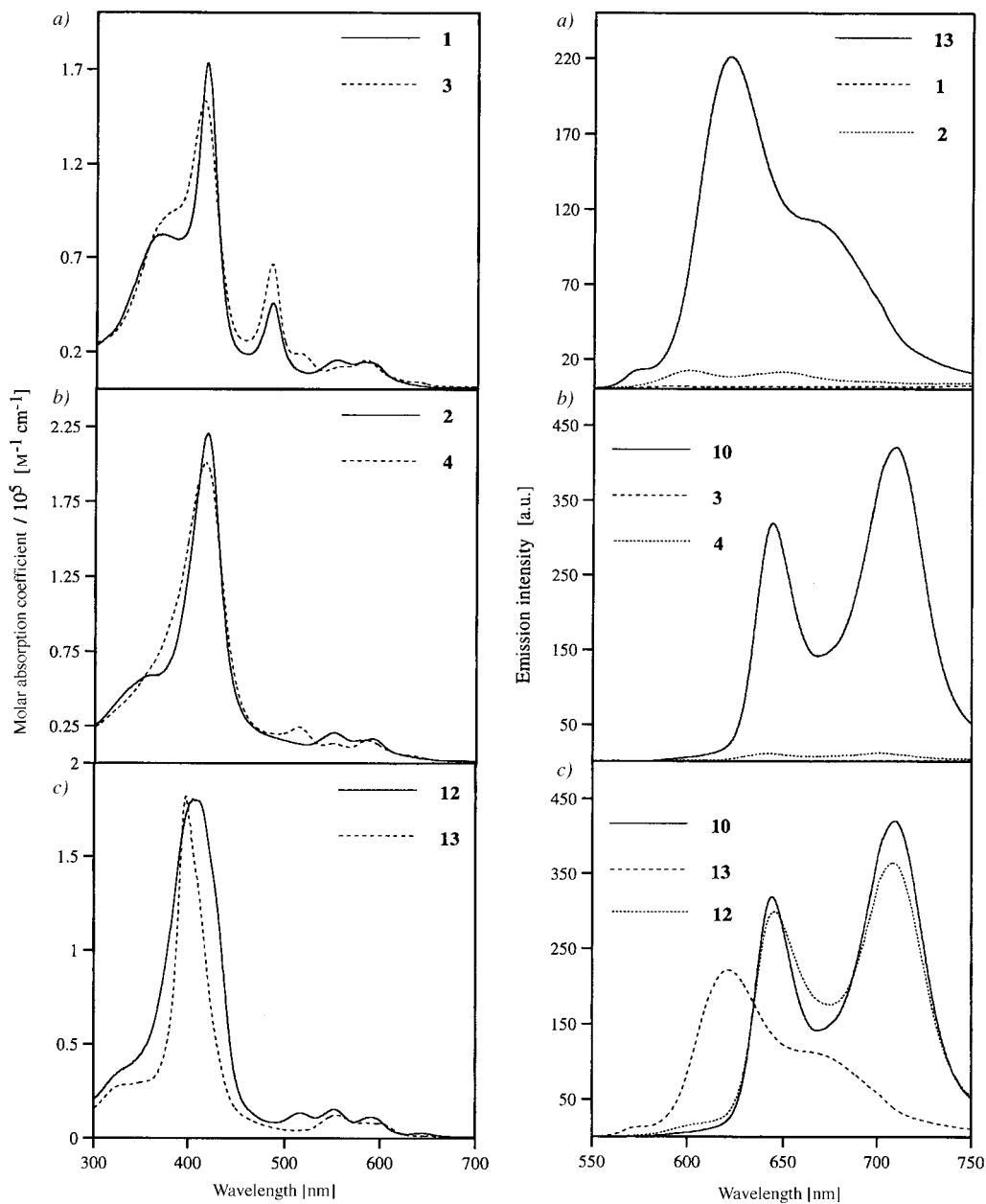
Fig. 1 (left). *UV/VIS Spectra* (CHCl₃) a) *manganese complexes* **1** (——) *and* **3** (– – – –), b) *iron complexes* **2** (——) *and* **4** (– – – –), *and* c) *zinc complexes* **12** (——) *and* **13** (– – – –)

Fig. 2 (right). *Emission spectra* (CHCl₃) *of* a) *heterometallic dimers* **1** (– – – –) *and* **2** (·····) *in comparison with dizinc dimer* **13** (——), b) *monometallic dimers* **3** (– – – –) *and* **4** (·····) *in comparison with bis(free-base) dimer* **10** (——), *and* c) *monozinc dimer* **12** (·····) *in comparison with bis(free-base) dimer* **10** (——) *and with dizinc dimer* **13** (——) (*normalized to the same chromophore unit concentration*)

[Fe^{III}(porphyrinato)] moiety. Since the reported free-energy-gap (ΔG) values [1a,e,k,m] for photo-induced electron transfer from the [Zn(porphyrinato)] to the [Fe(porphyrinato)] or [Mn(porphyrinato)] moiety in various covalently linked dimers range from -0.9 to -1 eV, this reaction is highly exothermic, and is thus likely to occur. The origin of the more efficient fluorescence quenching of Mn dimers **1** and **3** compared to that of Fe dimers **2** and **4** may be a result of the differences in solvation modes and ratio of '*anti*'/non-'*anti*' conformational population due to the flexibility of the covalent ethanediyl bridge, since the ΔG values are essentially the same for both metal complexes [1k]. An appearance of weaker emission of the monometallated dimers **3** and **4** in comparison with that of the bimetallic dimers **1** and **2** is possibly due to the same reason, because this effect is in contrast to the general tendency of enhanced electron-transfer efficiency and, consequently, fluorescence quenching for [Zn(porphyrinato)]-containing donor-acceptor systems due to the larger $-\Delta G$ values [23].

Table 2. *Steady-State Fluorescence Spectroscopic Data*[a])

Dimer	λ_{ex}[b]) [nm]	Q$^*_{X00}$-Band		Q$^*_{X01}$-Band		Photo-induced process
		λ_{em}[nm]	$I_{em}/I_{ref} \cdot 10^{-2}$	λ_{em}[nm]	$I_{em}/I_{ref} \cdot 10^{-2}$	
10	418	644	100	710	100	emission
13	398	622	100	665	100	emission
2[c])	418	600	6	649	10	electron transfer
4[d])	417	642	3	701	3	electron transfer
1[c])	417	592	1	651	2	electron transfer
3[d])	414	645	>1	702	>1	electron transfer
12[d])	406	646	94 (H$_2$ + Zn)	708	87 (H$_2 \gg$ Zn)	energy transfer
12[c])	406	622	15 (Zn $\gg$ H$_2$)			

[a]) $c = 10^{-6}$ mol l^{-1} in CHCl$_3$. [b]) λ_{ex} corresponds to the maximum of the B (*Soret*)-band. [c]) The reference is **13**. [d]) The reference is **10**.

Reflecting the differences in spatial orientation described above, the positions of the Q$^*_{X00}$- and Q$^*_{X01}$-bands of the '*syn*'-dimer **13** are red-shifted in comparison with those of the '*anti*'-dimers **1** and **2** by 30 and 22 nm for the Q$^*_{X00}$-band and by 14 and 16 nm for the Q$^*_{X01}$-band, respectively (*Table 2*). These shifts are due to strong interporphyrin interactions in the 'face-to-face' conformation of **13**. Similar bathochromic shifts of porphyrin fluorescence bands have been observed for covalently linked cofacial porphyrin dimers [18c,d] and stacked porphyrin aggregates [21a][24].

The fluorescence spectrum of the heterodimer **12** (*Fig. 2,c*) is dominated by emission from the free-base component (*ca.* 97%) with a small contribution from the Zn moiety. However, a precise determination of the residual Zn-component contribution by steady-state fluorescence spectroscopy is difficult because of the superimposed spectra of the [Zn(porphyrinato)] and free-base porphyrin moieties, and the different conformations of the Zn-containing dimers **12** and **13** and the bis(free-base) dimer **10**. The excitation spectrum of **12** (*Fig. 3*) is especially distinguishable from the absorption spectrum in the B-band region, while Q-bands of both spectra are nearly identical. The *Soret* band in the excitation spectrum of heterodimer **12** is red-shifted by 11 nm in comparison to the absorption spectrum, but is very similar to the same absorption band of the free-base homodimer **10**. This is possibly due to '*syn*'/'*anti*'
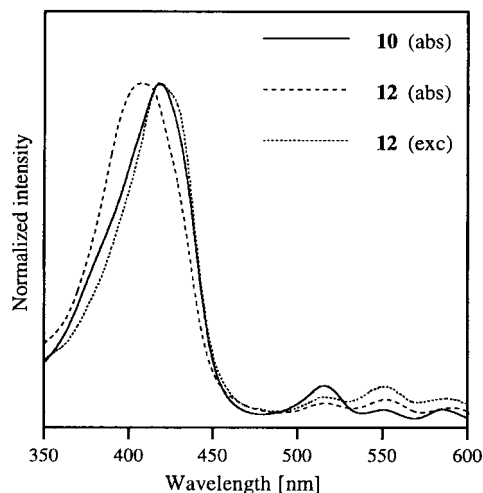
Fig. 3. *Excitation spectrum* (CHCl₃) *of monozinc dimer* **12** (·····) *in comparison with normalized absorption spectra of monozinc dimer* **12** (– – – –) *and bis(free-base) dimer* **10** (———)

conformational changes during excitation. These data are consistent with a very efficient energy transfer ($> 90\%$) from the S_1 state of the [Zn(porphyrinato)] moiety to the corresponding S_1 state of the free-base porphyrin component. Indeed, the positive difference of the S_1 levels between the [Zn(porphyrinato)] and free-base porphyrins moiety is favorable for this process, which has been observed for a variety of covalently linked Zn/free-base dimers [2a–j,l–o].

Further time-resolved spectroscopic measurements to reveal detailed mechanisms and parameters of photoinduced electron- and energy-transfer, as well as conformational changes in these heterodimers, are currently in progress and will be the subject of future reports from our group.

3. Conclusions. – Simple, selective metallation/demetallation procedures were developed and used to synthesize novel Mn- and Fe-containing heterodimers **1 – 4** linked by an ethanediyl bridge. A new general approach to transition-metal insertion into the porphyrin core by this methodology was developed and should be successfully applied to the metallation of porphyrin dimers. By means of ¹H-NMR (**12** and **13**), UV/ VIS, and fluorescence spectroscopy (**1 – 4**, **12** and **13**), it was shown that heterodimers **1 – 4** adopt mostly an '*anti*' form, while dizinc and monozinc dimers **12** and **13** are predominantly in the '*syn*' conformation. Fluorescence measurements clearly indicated that the efficient electron- or energy-transfer processes occur upon excitation of the dimers **1 – 4** and **12**, respectively.

Experimental Part

General. The reagents, reference metalloporphyrins, and solvents of an appropriate grade for reactions and spectroscopic measurements were purchased from either *Wako Chemicals Co.* or *Aldrich Chemical Co.* and were used as received. FeCl₂ or MnCl₂ (99.998 and 99.999% purity, resp.; *Aldrich*) were used in the metallation reactions. Column chromatography (CC): silica gel (*Wakogel C-200*). TLC (monitoring and purity control):

silica gel *60* (*Merck*). UV/VIS Spectra: *JASCO-V-560* and *Shimadzu-UV-3101PC* spectrophotometers; in CHCl$_3$ (spectral grade); λ_{max} (log ε) in nm. Steady-state fluorescence spectra: *Hitachi F-4500* fluorescence spectrophotometer, with correction for the spectral response of the instrument; excitation and emission slit widths, 5 nm; excitation wavelength at the maximum for the corresponding porphyrin B (*Soret*) band when obtaining emission spectra; emission monitoring at 646 nm (maximum of Q$^*_{X00}$-band) for the excitation spectrum of the monozinc dimer **12**, in CHCl$_3$ (spectral grade). ^{1}H-NMR Spectra: *Jeol-JNM-EX-400* spectrometer; at 400 MHz, δ in ppm, internally referenced to the residual proton resonance of CDCl$_3$ (δ 7.25), *J* in Hz. MS: *Jeol-JMS-DX303* mass spectrometer; FAB with Xe atoms (energy 6 keV, accelerating voltage 3 kV) in 3-nitrobenzyl alcohol (NBA) matrix; *m/z* (rel. %).

Transition-Metal Incorporation into Porphyrins: General Method Demonstrated with 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphyrin (H$_2$oep). To a soln. of H$_2$oep (5 mg, 0.01 mmol) in CHCl$_3$ (3 ml), FeCl$_2$ or MnCl$_2$ (20 mg, 0.16 mmol) in MeOH (2 ml) and two drops of 2,6-dimethylpyridine were added. The mixture was stirred at r.t. and monitored by TLC until the reaction was complete. Identification of the products was achieved by a comparison of the R_f value and UV/VIS spectrum with those of the purchased reference sample. The reaction conditions for various porphyrins are shown in *Table 1*.

5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin] (**10**). POCl$_3$ (26 ml) was added dropwise to anh DMF (22 ml) at 0°. A crystalline *Vilsmeier* complex was formed after 30 min, and (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrinato) copper (**6**; 710 mg, 1.19 mmol) in anh. 1,2-dichloroethane (500 ml) was added. The mixture was stirred at 60° for 45 min and monitored by TLC (silica gel, CHCl$_3$/MeOH, 100:1; appearance of **7** as green spot, R_f 0.00). After **6** had reacted fully, the mixture was poured into ice, the org. phase washed with cold H$_2$O (3 × 500 ml), dried (Na$_2$SO$_4$), and evaporated, and the residue dried *in vacuo* to give the intermediate imino salt **7**. Without purification, **7** was dissolved in anh. CHCl$_3$/MeOH 3:1 (500 ml) to which NaBH$_4$ (1.2 g) was added. The mixture was stirred for 20 min and monitored by TLC (silica gel, CHCl$_3$/MeOH 100:1). During this time, the color of the soln. changed from green to red. The mixture was then washed with H$_2$O (3 × 500 ml), the org. phase dried (Na$_2$SO$_4$) and evaporated, and the residue submitted to CC (silica gel (3.4 × 37 cm), CHCl$_3$ (removal of minor impurities), then CHCl$_3$/MeOH 100:1. The major product was dried *in vacuo* to give 689 mg (88.2%) of **8**. This was then refluxed in a mixture of MeI (35 ml; distilled over P$_2$O$_5$) and anh. CH$_2$Cl$_2$ (140 ml) for 3 h, and the reaction was monitored by TLC (silica gel, CCl$_4$; appearance of nonpolar **9**). The solvent was evaporated and the residue submitted to CC (silica gel (6.4 × 40 cm), CCl$_4$). The major product was dried *in vacuo* to give 422 mg (66.7%) of **9**, which was stirred in conc. H$_2$SO$_4$ soln. (90 ml) for 3.5 h before being poured into ice. This mixture was neutralized with NH$_3$ soln. and extracted with CHCl$_3$ (500 ml), the org. phase washed with H$_2$O (3 × 500 ml), dried (Na$_2$SO$_4$), and evaporated, and the residue submitted to CC (silica gel (6.4 × 40 cm), CHCl$_3$). The major product was dried *in vacuo* to give 375 mg of **10** (99%, or 58.2% based on **6**). Simultaneously, 4 mg (1%) of partially demetallated heterodimer **11** was separated. **10**: UV/VIS: 638 (3.50), 585 (4.09), 551 (4.08), 516 (4.45), 418 (*Soret*, 5.36). ^{1}H-NMR (CDCl$_3$, 20°C): 9.87 (*s*, 2 H); 9.79 (*s*, 4 H); 4.98 (*s*, CH$_2$CH$_2$); 4.09 (*q*, *J* = 7.6, 4 MeC*H*$_2$); 4.07 (*q*, *J* = 7.6, 4 MeC*H*$_2$); 3.81 – 3.69 (*m*, 4 MeC*H*$_2$); 3.61 – 3.44 (*m*, 4 MeC*H*$_2$); 1.93 (*t*, *J* = 7.6, 4 *Me*CH$_2$); 1.91 (*t*, *J* = 7.6, 4 *Me*CH$_2$); 1.67 (*t*, *J* = 7.6, 4 *Me*CH$_2$); 1.09 (*t*, *J* = 7.6, 4 *Me*CH$_2$); −2.83 (*s*, 2 NH); −3.06 (*s*, 2 NH). FAB-MS (NBA): 1097 (12, [*M* + 3 H]), 1096 (27, [*M* + 2 H]$^+$), 1095 (34, [*M* + H]$^+$), 1094 (6, *M*$^+$), 1093 (3, [*M* − H]$^+$), 550 (13, [1/2*M* + 3 H]$^+$), 549 (46, [1/2*M* + 2 H]$^+$), 548 (100, [1/2*M* + H]$^+$), 547 (64, 1/2*M*$^+$), 546 (18, [1/2*M* − H]$^+$).

{{5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrinato](2−)}-κN^{21},κN^{22},κN^{23},κN^{24}}zinc (**12**) *and {μ-{{5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrinato](4−)}-κN^{21},κN^{22}, κN^{23},κN^{24}:κN$^{21′}$,κN$^{22′}$,κN$^{23′}$,κN$^{24′}$}}dizinc* (**13**). A MeOH soln. of Zn(OAc)$_2$·2 H$_2$O (19 ml, 2 g/l) was added dropwise to a refluxing soln. of **10** (160 mg, 0.15 mmol) in CH$_2$Cl$_2$ (200 ml) within 4.5 h (TLC monitoring (silica gel, CHCl$_3$/MeOH 100:1); R_f 0.09 (**10**), 0.21 (**12**), 1.00 (**13**)). The soln. was then evaporated and the residue submitted to CC (silica gel (3.4 × 45 cm), CHCl$_3$). The second major band gave a residue that was dried *in vacuo*: 91 mg of **12** (60% based on reacted **10**). The first band gave 35 mg (22%) of **13** which was subjected to subsequent demetallation to recover initial **10** (see below). The third band yielded 17 mg of non-reacted **10**.

Data of **12**: UV/VIS (CHCl$_3$): 642 (3.41), 590 (4.05), 552 (4.19), 516 (4.12), 406 (*Soret*, 5.26), 334 (sh, 4.57). ^{1}H-NMR (CDCl$_3$, 20°C): 9.84 (*s*, 1 H); 9.72 (*s*, 1 H); 8.81 (*s*, 2 H); 8.74 (*s*, 2 H); 5.29 ('*t*', C*H*$_2$CH$_2$); 4.98 ('*t*', C*H*$_2$CH$_2$); 4.30 – 3.80 (*m*, 7 MeC*H*$_2$); 3.80 – 3.60 (*m*, 1 MeC*H*$_2$); 3.60 – 3.45 (*m*, 1 MeC*H*$_2$); 3.45 – 3.30 (*m*, 1 MeC*H*$_2$); 3.30 – 3.10 (*m*, 2 MeC*H*$_2$); 3.10 – 2.95 (*m*, 2 MeC*H*$_2$); 2.90 – 2.70 (*m*, 2 MeC*H*$_2$); 1.94 (*t*, *J* = 7.3, 2 *Me*CH$_2$); 1.93 (*t*, *J* = 7.3, 2 *Me*CH$_2$); 1.73 ('*dt*', 4 *Me*CH$_2$); 1.44 (*t*, *J* = 7.3, 2 *Me*CH$_2$); 1.24 (*t*, *J* = 7.3, 2 *Me*CH$_2$); 1.15 ('*t*', 4 *Me*CH$_2$); −4.33 (*s*, NH); −4.91 (br. *s*, NH). FAB-MS (NBA): 1163 (11, [*M* + 6]$^+$), 1162 (17, [*M* + 5]$^+$), 1161 (19, [*M* + 4]$^+$), 1160 (25, [*M* + 3]$^+$), 1159 (25, [*M* + 2]$^+$), 1158 (28, [*M* + 1]$^+$), 1157 (8, *M*$^+$), 1156 (4,

$[M-1]^+$), 614 (10, $[M-$oepCH$_2+4]^+$, 10), 613 ($[M-$oepCH$_2+3]^+$, 24), 612 ($[M-$oepCH$_2+2]^+$, 23), 611($[M-$oepCH$_2+1]^+$, 36), 610 ($[M-$oepCH$_2]^+$, 31), 609 ($[M-$oepCH$_2-1]^+$, 54), 608 ($[M-$oepCH$_2-2]^+$, 15), 607 ($[M-$oepCH$_2-3]^+$, 11), 550 ($[M-$ZnoepCH$_2+3]^+$, 18), 549 ($[M-$ZnoepCH$_2+2]^+$, 59), 548 ($[M-$ZnoepCH$_2+1]^+$, 100), 547 ($[M-$ZnoepCH$_2]^+$, 49), 546 ($[M-$ZnoepCH$_2-1]^+$, 15), 545 ($[M-$ZnoepCH$_2-2]^+$, 11).

Data of **13**: UV/VIS (CHCl$_3$): 598 (3.89), 585 (3.91), 555 (4.09), 398 (*Soret*, 5.26), 335 (sh, 4.45). ^{1}H-NMR (CDCl$_3$, 20°): 9.84 (*s*, 2 H); 8.18 (br. *s*, 4 H); 5.17 (*s*, CH_2CH_2); 4.32 – 4.26 (*m*, 2 MeCH_2); 4.10 – 4.05 (*m*, 2 MeCH_2); 3.91 – 3.85 (*m*, 2 MeCH_2); 3.73 – 3.67 (*m*, 2 MeCH_2); 3.36 – 3.29 (*m*, 2 MeCH_2); 3.11 – 3.06 (*m*, 2 MeCH_2); 2.64 – 2.57 (*m*, 2 MeCH_2); 2.45 – 2.40 (*m*, 2 MeCH_2); 1.94 (*t*, $J=7.6$, 4 MeCH$_2$); 1.64 (*t*, $J=7.6$, 4 MeCH$_2$); 1.44 (*t*, $J=7.3$, 4 MeCH$_2$); 1.06 ('*t*', 4 MeCH$_2$). FAB-MS (NBA): 1227 (3, $[M+7]^+$), 1226 (5, $[M+6]^+$), 1225 (7, $[M+5]^+$), 1224 (9, $[M+4]^+$), 1223 (11, $[M+3]^+$), 1222 (10, $[M+2]^+$), 1221 (10, $[M+1]^+$), 1220 (8, M^+), 1219 (6, $[M-1]^+$), 1218 (3, $[M-2]^+$), 615 (18, $[1/2M+5]^+$), 614 (47, $[1/2M+4]^+$), 613 (42, $[1/2M+3]^+$), 612 (70, $[1/2M+2]^+$), 611 (54, $[1/2M+1]^+$), 610 (100, $1/2M^+$), 609 (25 $[1/2M-1]^+$), 608 (17, $[1/2M-2]^+$).

Recovery of **10** *from* **13**. A CHCl$_3$ soln. (300 ml) of **13** (191 mg, 0.16 mmol) was vigorously shaken with 6M HCl (2 × 300 ml) in a separating funnel, then washed with H$_2$O (3 × 500 ml), dried (Na$_2$SO$_4$), and evaporated. The residue was dried *in vacuo:* 171 mg (*ca.* 100%) of pure **10**.

{μ-[[5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrinato](4−)]-κN^{21},κN^{22},κN^{23},κN^{24}: κN$^{21′}$,κN$^{22′}$,κN$^{23′}$,κN$^{24′}$]}(zinc)manganese(1+) Chloride (**1**). MnCl$_2$ (200 mg, 0.16 mmol) in MeOH (20 ml) and 2,6-dimethylpyridine (0.1 ml) were added to a soln. of **12** (104 mg, 0.09 mmol) in CHCl$_3$ (30 ml). The mixture was stirred for 8 h at r.t. (TLC monitoring (silica gel, CHCl$_3$/MeOH 100 : 1). The soln. was then evaporated and the residue submitted to CC (silica gel (4.8 × 20 cm), CHCl$_3$ (removal of **12**), then CHCl$_3$/MeOH 50 : 1). The product was recrystallized from CH$_2$Cl$_2$/heptane and dried *in vacuo:* 105 mg of **1** (*ca.* 100% based on reacted **12** at 94% conversion). UV/VIS (CHCl$_3$): 589 (4.15), 581 (4.16), 552 (4.19), 485 (4.66), 417 (*Soret*, 5.24), 370 (4.92), FAB-MS (NBA): 1216 (11, $[M+6]^+$), 1215 (27, $[M+5]^+$), 1214 (44, $[M+4]^+$), 1213 (48, $[M+3]^+$), 1212 (63, $[M+2]^+$), 1211 (63, $[M+1]^+$), 1210 (70, M^+), 1209 (13, $[M-1]^+$), 613 (37, $[M-$MnoepCH$_2)+3]^+$), 612 (31, $[M-$MnoepCH$_2+2]^+$), 611 (49, $[M-$MnoepCH$_2+1]^+$), 610 (35, $[M-$MnoepCH$_2]^+$), 609 (67, $[M-$MnoepCH$_2-1]^+$), 601 (51, $[M-$ZnoepCH$_2+1]^+$), 600 (100, $[M-$ZnoepCH$_2]^+$), 599 (44, $[M-$ZnoepCH$_2-1]^+$), 598 (26, $[M-$ZnoepCH$_2-2]^+$).

{μ-[[5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrinato](4−)]-κN^{21},κN^{22},κN^{23},κN^{24}: κN$^{21′}$,κN$^{22′}$,κN$^{23′}$,κN$^{24′}$]}(zinc)iron(1+) Chloride (**2**) *and {μ-[[5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octa-ethyl-21H,23H-porphyrinato](4−)-κN^{21},κN^{22},κN^{23},κN^{24}:κN$^{21′}$,κN$^{22′}$,κN$^{23′}$,κN$^{24′}$]}diiron(2+) Dichloride* (**14**). FeCl$_2$ (200 mg, 0.16 mmol) in MeOH (20 ml) and 2,6-dimethylpyridine (0.1 ml) were added to a soln. of **12** (111 mg, 0.1 mmol) in CHCl$_3$ (30 ml). The mixture was stirred for 1 h at r.t. (TLC monitoring (silica gel, CHCl$_3$/MeOH 100 : 1)). The soln. was then evaporated and the residue submitted to CC (silica gel (4.8 × 27 cm), CHCl$_3$ (→ **2**), then CHCl$_3$/MeOH 50 : 1 (→ **14**)). Both **2** and **14** were further purified by CC (silica gel (6.4 × 53 cm for **2** and 4.8 × 25 cm for **14**), CHCl$_3$/MeOH 500 : 1 and 100 : 1, resp. The products were recrystallized from CH$_2$Cl$_2$/MeOH and dried *in vacuo:* 55 mg (46%) of **2** and 30 mg (25%) of **14**.

Data of **2**: UV/VIS (CHCl$_3$): 592 (4.21), 578 (4.19), 551 (4.31), 418 (*Soret*, 5.34), 363 (sh, 4.77). FAB-MS (NBA): 1216 (7, $[M+5]^+$), 1215 (11, $[M+4]^+$), 1214 (13, $[M+3]^+$), 1213 (16, $[M+2]^+$), 1212 (17, $[M+1]^+$), 1211 (16, M^+), 1210 (7, $[M-1]^+$), 615 (15, $[M-$FeoepCH$_2+5]^+$), 614 (21, $[M-$FeoepCH$_2+4]^+$), 613 (43, $[M-$FeoepCH$_2+3]^+$), 612 (34, $[M-$FeoepCH$_2+2]^+$), 611 (57, $[M-$FeoepCH$_2+1]^+$), 610 (42, $[M-$FeoepCH$_2]^+$), 609 (80, $[M-$FeoepCH$_2-1]^+$), 608 (17, $[M-$FeoepCH$_2-2]^+$), 607 (16, $[M-$FeoepCH$_2-3]^+$), 603 (15, $[M-$ZnoepCH$_2+2]^+$), 602 (46, $[M-$ZnoepCH$_2+1]^+$), 601 (100, $[M-$ZnoepCH$_2]^+$), 600 (30, $[M-$ZnoepCH$_2-1]^+$), 599 (32, $[M-$ZnoepCH$_2-2]^+$), 598 (14, $[M-$ZnoepCH$_2-3]^+$), 597 (16, $[M-$ZnoepCH$_2-4]^+$).

Data of **14**: UV/VIS (CHCl$_3$): 618 (3.83), 580 (4.04), 404 (*Soret*, 4.96), 349 (sh, 4.74). FAB-MS (NBA): 1357 (5, $[M+$NBA$+2]^+$), 1356 (9, $[M+$NBA$+1]$), 1355 (10, $[M+$NBA$]^+$), 1354 (3, $[M+$NBA$-1]^+$), 1205 (7, $[M+3]^+$), 1204 (14, $[M+2]^+$), 1203 (17, $[M+1]^+$), 1202 (7, M^+), 1201 (4, $[M-1]^+$), 602 (100, $[1/2M+1]^+$), 601 (52, $1/2M^+$), 600 (34, $[1/2M-1]^+$), 599 (23, $[1/2M-2]^+$), 598 (9, $[1/2M-3]^+$).

{[5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrinato](2−)]-κN^{21},κN^{22},κN^{23},κN^{24}]-manganese(1+) Chloride (**3**). A soln. of **1** (8 mg, 0.006 mmol) in CHCl$_3$ (20 ml) was vigorously shaken 3 times with 2M HCl (50 ml) in a separatory funnel, then washed with H$_2$O (3 × 50 ml) until pH 7 was reached, before being dried (Na$_2$SO$_4$) and evaporated. The residue was submitted to CC (silica gel (4.8 × 29 cm) CHCl$_3$/MeOH 50 : 1). The product was recrystallized from CH$_2$Cl$_2$/MeOH and dried *in vacuo:* 7.2 mg (95%) of **3**. UV/VIS (CHCl$_3$): 633 (3.59), 584 (4.19), 553 (4.08), 513 (4.28), 484 (4.82), 414 (*Soret*, 5.19), 383 (sh, 4.98). FAB-MS

(NBA): 1151 (12, $[M+4]^+$), 1150 (39, $[M+3]^+$), 1149 (83, $[M+2]^+$), 1148 (100, $[M+1]^+$), 1147 (18, M^+), 1146 (7, $[M-1]^+$), 603 (6, $[M-\text{oepCH}_2+3]^+$), 602 (25, $[M-\text{oepCH}_2+2]^+$), 601 (53, $[M-\text{oepCH}_2+1]^+$), 600 (20, $[M-\text{oepCH}_2]^+$), 599 (12, $[M-\text{oepCH}_2-1]^+$), 550 (6, $[M-\text{MnoepCH}_2+3]^+$), 549 (13, $[M-\text{MnoepCH}_2+2]^+$), 548 (26, $[M-\text{MnoepCH}_2+1]^+$), 547 (5, $[M-\text{MnoepCH}_2]^+$).

*{{5,5′-(Ethane-1,2-diyl)bis[2,3,7,8,12,13,17,18-octaethyl-21*H,23H-*porphyrinato](2-)}-κN²¹,κN²²,κN²³,κN²⁴]i-ron(1+) Chloride* (**4**). As described for **3**, **2** (12.3 mg, 0.01 mmol) in CHCl₃ (30 ml) was treated with 2м HCl (50 ml). CC (silica gel (4.8 × 29 cm), CHCl₃/MeOH 300 : 1), recrystallization from CH₂Cl₂/MeOH, and drying *in vacuo* gave 11.6 mg of **9** (*ca.* 100%). UV/VIS (CHCl₃): 633 (3.68), 586 (4.19), 550 (4.12), 514 (4.39), 417 (*Soret*, 5.30). FAB-MS (NBA): 1153 (8, $[M+5]^+$), 1152 (25, $[M+4]^+$), 1151 (55, $[M+3]^+$), 1150 (76, $[M+2]^+$), 1149 (31, $[M+1]^+$), 1148 (16, M^+), 1147 (6, $[M-1]^+$), 604 (12, $[M-\text{oepCH}_2+3]^+$), 603 (45, $[M-\text{oepCH}_2+2]^+$), 602 (100, $[M-\text{oepCH}_2+1]^+$), 601 (24, $[M-\text{oepCH}_2]^+$), 600 (22, $[M-\text{oepCH}_2-1]^+$), 551 (9, $[M-\text{FeoepCH}_2+4]^+$), 550 (26, $[M-\text{FeoepCH}_2+3]^+$), 549 (35, $[M-\text{FeoepCH}_2+2]^+$), 548 (45, $[M-\text{FeoepCH}_2+1]^+$), 547 (9, $[M-\text{FeoepCH}_2]^+$), 546 (9, $[M-\text{FeoepCH}_2-1]^+$).

REFERENCES

[1] a) P. J. F. de Rege, S. A. Williams, M. J. Therien, *Science (Washington, D.C.)* **1995**, *269*, 1409; b) A. Helms, D. Heiler, G. McLendon, *J. Am. Chem. Soc.* **1992**, *114*, 6227; c) A. Helms, D. Heiler, G. McLendon, *ibid.* **1991**, *113*, 4325; d) A. Helms, G. McLendon, P. Rogalskyj, *ibid.* **1987**, *109*, 604; e) A. Osuka, K, Maruyama, N. Mataga, T. Asahi, I. Yamazaki, N. Tamai, *ibid.* **1990**, *112*, 4958; f) M. Linke, J.-C. Chambron, V. Heitz, J.-P. Sauvage, *ibid.* **1997**, *119*, 11329; g) J.-C. Chambron, A. Harriman, V. Heitz, J.-P. Sauvage, *ibid.* **1993**, *115*, 6109; h) A. M. Brun, S. J. Atherton, A. Harriman, V. Heitz, J.-P. Sauvage, *ibid.* **1992**, *114*, 4632; i) A. M. Brun, A. Harriman, V. Heitz, J.-P. Sauvage, *ibid.* **1991**, *113*, 8657; j) A. Lamrabte, J. M. Janot, E. Bienvenue, M. Momenteau, P. Seta, *Photochem. Photobiol.* **1991**, *54*, 123; k) N. Mataga, H. Yao, T. Okada, Yu. Kanda, A. Harriman, *Chem. Phys.* **1989**, *131*, 473; l) R. L. Brookfield, H. Ellul, A. Harriman, *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1837; m) I. Fujita, T. L. Netzel, C. K. Chang, C.-B. Wang, *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 413.
[2] a) R. W. Wagner, J. Seth, S. I. Yang, D. Kim, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Org. Chem.* **1998**, *63*, 5042; b) P. G. Van Patten, A. P. Shreve, J. S. Lindsey, R. J. Donohoe, *J. Phys. Chem. B* **1998**, *102*, 4209; c) J.-P. Strachan, S. Gentemann, J. Seth, W. A. Kalsbeck, J. S. Lindsey, D. Holten, D. F. Bocian, *Inorg. Chem.* **1998**, *37*, 1191; d) J.-P. Strachan, S. Gentemann, J. Seth, W. A. Kalsbeck, J. S. Lindsey, D. Holten, D. F. Bocian, *J. Am. Chem. Soc.* **1997**, *119*, 11191; e) N. Nishino, R. W. Wagner, J. S. Lindsey, *J. Org. Chem.* **1996**, *61*, 7534; f) J. Seth, V. Palaniappan, T. E. Johnson, S. Prathapan, J. S. Lindsey, D. F. Bocian, *J. Am. Chem. Soc.* **1994**, *116*, 10578; g) S. Prathapan, T. E. Johnson, J. S. Lindsey, *ibid.* **1993**, *115*, 7519; h) M. E. Baraka, J. M. Janot, L. Ruhlmann, A. Giraudeau, M. Deumie, P. Seta, *J. Photochem. Photobiol., A* **1998**, *113*, 163; i) U. Rempel, S. Meyer, B. von Maltzan, C. von Borczyskowski, *J. Lumin.* **1998**, *78*, 97; j) K. K. Jensen, S. B. van Berlekom, J. Kajanus, J. Mårtensson, B. Albinsson, *J. Phys. Chem. A* **1997**, *101*, 2218; k) M. Asano-Someda, T. Ichino, Y. Kaizu, *ibid.* **1997**, *101*, 4484; l) H. Tamiaki, T. Miyatake, R. Tanikaga, A. R. Holzwarth, K. Schaffner, *Angew. Chem.* **1996**, *108*, 810; *ibid., Int. Ed. Engl.* **1996**, *35*, 772; m) M. Raghavan, V. Krishnan, *Chem. Phys. Lett.* **1993**, *205*, 19; n) A. Osuka, T. Nagata, F. Kobayashi, R. P. Zhang, K. Maruyama, N. Mataga, T. Asahi, T. Ohno, K. Nozaki, *ibid.* **1992**, *199*, 302; o) J. L. Sessler, M. R. Johnson, T.-Y. Lin, S. E. Creager, *J. Am. Chem. Soc.* **1988**, *110*, 3659; p) E. I. Zen'kevich, A. M. Shul'ga, A. B. Chernook, E. I. Sagun, G. P. Gurinovich, *Russ. Chem. Phys.* **1989**, *8*, 842; q) E. I. Zen'kevich, A. M. Shul'ga, A. B. Chernook, G. P. Gurinovich, *Russ. J. Appl. Spectrosc.* **1986**, *45*, 790.
[3] a) K.-I. Sugiura, G. Ponomarev, S. Okubo, A. Tajiri, Y. Sakata, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1115; b) T. Arai, K. Takei, N. Nishino, T. Fujimoto, *Chem. Commun.* **1996**, 2133; c) A. El-Kasmi, D. Lexa, P. Maillard, M. Momenteau, J.-M. Savéant, *J. Phys. Chem.* **1993**, *97*, 6090; d) J. L. Sessler, V. L. Capuano, *Tetrahedron Lett.* **1993**, *34*, 2287; e) R. Guilard, M. A. Lopez, A. Tabard, P. Richard, C. Lecomte, S. Brandes, J. E. Hutchison, J. P. Collman, *J. Am. Chem. Soc.* **1992**, *114*, 9877.
[4] a) R. Guilard, S. Brandes, A. Tabard, N. Bouhmaida, C. Lecomte, P. Richard, J.-M. Latour, *J. Am. Chem. Soc.* **1994**, *116*, 10202; b) Y. Naruta, M. Sasayama, K. Maruyama, *Chem. Lett.* **1992**, 1267; c) Y. Naruta, K. Maruyama, *J. Am. Chem. Soc.* **1991**, *113*, 3595.
[5] R. W. Wagner, J. S. Lindsey, J. Seth, V. Palaniappan, D. F. Bocian, *J. Am. Chem. Soc.* **1996**, *118*, 3996; R. W. Wagner, J. S. Lindsey, *ibid.* **1994**, *116*, 9759.

[6] T. Takemura, S. Nakajima, I. Sakata, *Photochem. Photobiol.* **1994**, *59*, 366.

[7] R. Paolesse, R. K. Pandey, T. P. Forsyth, L. Jaquinod, K. R. Gerzevske, D. J. Nurco, M. O. Senge, S. Licoccia, T. Boschi, K. M. Smith, *J. Am. Chem. Soc.* **1996**, *118*, 3869; R. K. Pandey, T. P. Forsyth, K. R. Gerzevske, J. J. Lin, K. M. Smith, *Tetrahedron Lett.* **1992**, *33*, 5315; D. B. Amabilino, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 3285; J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.* **1992**, 1131; V. Heitz, S. Chardon-Noblat, J.-P. Sauvage, *Tetrahedron Lett.* **1991**, *32*, 197; E. E. Bonfantini, D. L. Officer, *ibid.* **1993**, *34*, 8531; J. Mårtensson, K. Sandros, O. Wennerström *ibid.* **1993**, *34*, 541; Yu. V. Ishkov, Z. I. Zhilina, Zh. V. Grushevaya, I. S. Voloshansky, *Russ. J. Org. Chem.* **1990**, *26*, 2433.

[8] a) T. E. Clement, D. J. Nurco, K. M. Smith, *Inorg. Chem.* **1998**, *37*, 1150; b) X. Zhou, K. S. Chan, *J. Org. Chem.* **1998**, *63*, 99; c) H. Higuchi, M. Takeuchi, J. Ojima, *Chem. Lett.* **1996**, 593; d) G. V. Ponomarev, V. V. Borovkov, A. M. Shul'ga, Y. Sakata, *J. Chem. Soc., Chem. Commun.* **1994**, 1927; e) A. M. Shul'ga, G. V. Ponomarev, *Russ. Chem. Heterocycl. Comp.* **1988**, 339; f) S. Chardon-Noblat, J.-P. Sauvage, *Tetrahedron Lett.* **1991**, *32*, 5123; g) A. Osuka, S. Marumo, N. Konishi, K. Maruyama, I. Yamazaki, T. Yamazaki, Y. Shirakawa, Y. Nishimura, *Chem. Lett.* **1993**, 2141; h) A. Osuka, Y. Ikawa, K. Maruyama, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3322.

[9] T. Nagata, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 385; A. Osuka, T. Nagata, K. Maruyama, *Chem. Lett.* **1991**, 1687.

[10] For recent reviews, see H. Kurreck, M. Huber, *Angew. Chem.* **1995**, *107*, 929; *ibid., Int. Ed. Engl.* **1995**, *34*, 849; M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435.

[11] J. W. Buchler, in 'Porphyrins and Metalloporphyrins', Ed. K. M. Smith, Elsevier, Amsterdam, 1975, pp. 157–231.

[12] For the comprehensive review, see 'Metalloporphyrin Catalyzed Oxidations', Eds. F. Montanari and L. Casella, Kluwer, Dordrecht, 1994.

[13] For a preliminary communication, see V. V. Borovkov, J. M. Lintuluoto, Y. Inoue, *Synlett* **1998**, 768.

[14] V. V. Borovkov, J. M. Lintuluoto, Y. Inoue, *Synlett* **1999**, 61.

[15] D. V. Yashunsky, G. V. Ponomarev, D. P. Arnold, *Tetrahedron Lett.* **1996**, *37*, 7147; M. O. Senge, G. V. Ponomarev, T. P. Forsyth, K. M. Smith, *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1644.

[16] S. Vilain-Deshayes, A. Robert, P. Maillard, B. Meunier, M. Momenteau, *J. Mol. Catal. A: Chem.* **1996**, *113*, 23; S. Banfi, A. Manfredi, F. Montanari, G. Pozzi, S. Quici, *ibid.* **1996**, *113*, 77; J. P. Collman, V. J. Lee, C. J. Kellen-Yuen, X. Zhang, J. A. Ibers, J. I. Brauman, *J. Am. Chem. Soc.* **1995**, *117*, 692; D. Pattou, G. Labat, S. Defrance, J.-L. Séris, B. Meunier, *Bull. Soc. Chim. Fr.* **1994**, *131*, 78; K. Ohkubo, T. Sagawa, Y. Minamoto, *J. Mol. Catal.* **1994**, *91*, 7; I. Artaud, K. Ben-Aziza, D. Mansuy, *J. Org. Chem.* **1993**, *58*, 3373; A. Robert, B. Loock, M. Momenteau, B. Meunier, *Inorg. Chem.* **1991**, *30*, 706; A. El-Kasmi, D. Lexa, P. Maillard, M. Momenteau, J.-M. Savéant, *J. Am. Chem. Soc.* **1991**, *113*, 1586; D. R. Leanord, J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2* **1990**, 1917; E. Tsuchida, T. Komatsu, E. Hasegawa, H. Nishide, *J. Chem. Soc., Dalton Trans.* **1990**, 2713; P. Maillard, C. Schaeffer, C. Huel, J.-M. Lhoste, M. Momenteau, *J. Chem. Soc., Perkin Trans. 1* **1988**, 3285; J. T. Groves, R. S. Myers, *J. Am. Chem. Soc.* **1983**, *105*, 5791; J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, W. T. Robinson, *ibid.* **1975**, *97*, 1427.

[17] G. V. Ponomarev, D. V. Yashunsky, V. V. Borovkov, Y. Sakata, D. Arnold, *Russ. Chem. Heterocycl. Comp.* **1997**, 1627.

[18] a) G. V. Ponomarev, V. V. Borovkov, K.-i. Sugiura, Y. Sakata, A. M. Shul'ga, *Tetrahedron Lett*, **1993**, *34*, 2153; b) M. O. Senge, K. R. Gerzevske, M. G. H. Vicente, T. P. Forsyth, K. M. Smith, *Angew. Chem.* **1993**, *105*, 745; *ibid., Int. Ed. Engl.* **1993**, *32*, 750; c) A. Osuka, S. Nakajima, K. Maruyama, *J. Org. Chem.* **1992**, *57*, 7355; d) A. Osuka, S. Nakajima, T. Nagata, K. Maruyama, K. Toriumi, *Angew. Chem.* **1991**, *103*, 579; *ibid., Int. Ed. Engl.* **1991**, *30*, 582; e) R. Karaman, A. Blaskó, Ö. Almarsson, R. Arasasingham, T. C. Bruice, *J. Am. Chem. Soc.* **1992**, *114*, 4889; f) B. C. Bookser, T. C. Bruice, *ibid.* **1991**, *113*, 4208.

[19] M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371.

[20] V. S.-Y. Lin, S. G. DiMagno, M. J. Therien, *Science (Washington, D.C.)* **1994**, *264*, 1105; H. L. Anderson, *Inorg. Chem.* **1994**, *33*, 1191; J. J. Gosper, M. Ali, *J. Chem. Soc., Chem. Commun.* **1994**, 1707; d) A. Osuka, N. Tanabe, R.-P. Zhang, K. Maruyama, *Chem. Lett.* **1993**, 1505.

[21] a) N. C. Maiti, S. Mazumdar, N. Reriasamy, *J. Phys. Chem. B* **1998**, *102*, 1528; b) C. Endisch, J.-H. Fuhrhop, J. Buschmann, P. Luger, U. Siggel, *J. Am. Chem. Soc.* **1996**, *118*, 6671; c) J. M. Ribó, J. Crusats, J.-A. Farrera, M. L. Valero, *J. Chem. Soc., Chem. Commun.* **1994**, 681; d) Y. Kobuke, H. Miyaji, *J. Am. Chem. Soc.* **1994**, *116*, 4111; e) D. L. Akins, H.-R. Zhu, C. Guo, *J. Phys. Chem.* **1994**, *98*, 3612; f) J. H. van Esch, M. C. Feiters, A.-M. P. Peters, R. J. M. Nolte, *ibid.* **1994**, *98*, 5541; g) J. H. van Esch, A.-M. P. Peters, R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.* **1990**, 638; h) T. Nagamura, T. Koga, T. Ogawa, *J. Photochem. Photobiol. A:*

Chem. **1992**, *66*, 119; i) G. A. Schick, I. C. Schreiman, R. W. Wagner, J. S. Lindsey, D. F. Bocian, *J. Am. Chem. Soc*. **1989**, *111*, 1344.

[22] V. V. Borovkov, J. M. Lintuluoto, Y. Inoue, *J. Phys. Chem.*, in press.

[23] V. V. Borovkov, R. P. Evstigneeva, L. N. Strekova, E. I. Filippovich, *Russ. Chem. Rev*. **1989**, *58*, 602.

[24] V. V. Borovkov, M. Anikin, K. Wasa, Y. Sakata, *Photochem. Photobiol*. **1996**, *63*, 477 and ref. cit. therein.