6052 *Inorg. Chem.* **1998,** *37,* 6052−6059

Manganese Porphyrin Heterodimers and -trimers in Aqueous Solution

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Received March 5, 1998

Noncovalent face-to-face heterodimers and -trimers between β-tetracationic and *meso*-tetraanionic manganese(III) porphyrins have been prepared in bulk water at pH 12. They are held together by Coulomb interactions between four β-methylpyridinium and *meso*-phenylsulfonate or *meso*-phenylcarboxylate ion pairs in eclipsed orientations. Spectroelectrochemistry has been used to characterize the redox products and to establish reversibility. UV−visible titrations indicate quantitative trimerization at concentrations $>10^{-5}$ M. Cyclic voltammetry shows that all three Mn(III) ions were oxidized simultaneously to Mn(IV) at potentials close to 300 mV at pH 12. Electroreduction to Mn(II) was often not observed in the trimers, although the monomers reacted readily under the same conditions. Quantitative chemical reduction of Mn(III) to Mn(II) porphyrin trimers was, however, achieved with dithionite. Trimers containing three paramagnetic Mn(II) or Mn(IV) ions are thus easily accessible. The heterodimers and -trimers and homodimers also catalyzed the formation of dioxygen by electrooxidation of Mn(III) to Mn(IV) between 0.6 and 2.0 V while at pH 12.

Introduction

The four-electron oxidation of water to dioxygen in photosynthetic organisms by photosystem II (PS II) takes place in a oxygen evolving complex (OEC) in which manganese proteins play the central catalytic role. Two or four manganese ions may be directly involved in this process.[1,2] In model systems with manganese porphyrins, the manganese(V) oxo group has emerged as a key precursor of dioxygen formation.[3] Two such porphyrins are needed, and they should interact to allow four-electron transfers. We propose noncovalent heterodimers in water, which have so far only been studied on the case of meso-substituted cationic and anionic porphyrin[4] and optimized phthalocyanine−porphyrin dimers.[5]

We have recently reported on water-soluble porphyrin heterodimers and -trimers with a binding constant on the order of 10^7 M^{-1}. One of the components bears phenylsulfonate or -carboxylate anions in the meso positions, its partner has four *N*-methylpyridinium substituents on the β-pyrrolic positions, together with four ethyl substituents in the cationic component, which prevent polymerization and consequent precipitation. Only A−B dimers and A−B−A trimers are formed efficiently.[6,7] Such molecular assemblies should be as useful for catalytic purposes involving multielectron transfer, e.g., the formation or removal of molecular oxygen in aqueous solutions as covalent dimers.[8] Furthermore, one might think to use one porphyrin in the trimer as an antenna for a redox-active metalloporphyrin, provided the latter has useful catalytic properties.

In the following, we describe first experiments with noncovalent manganese porphyrinate heterodimers and -trimers. The most important aspects of this investigation are the findings that (i) Coulomb heterodimers and -trimers in water survive the introduction of axial ligands to central metal ions and (ii) that multivalent manganese porphyrinates [e.g., Mn(III)−Mn(IV)−Mn(III)] are not accessible.

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10.1021/ic980241w CCC: $15.00

Experimental Section

(β-Tetraethyl-β-tetrakis(1-methyl-4-pyridinium)porphyrinato)manganese(III) Pentachloride (1). β-Tetraethyl-β-tetrakis(1-methyl-4-pyridinium)porphyrin (isomers **III** and **IV**; 150 mg, 200 μmol) prepared as previously reported[6,7] and 63 mg (500 μmol) of manganese(II) acetate tetrahydrate were dissolved in 15 mL of *N,N*-dimethylformamide (DMF). The mixture was heated to 140 °C for 3 h. After it was cooled to 20 °C, the reaction mixture was concentrated to a few milliliters. Acetate buffer (acetic acid/sodium acetate, 1:1; 30 mL of 0.1 M) was added, and the precipitate collected, washed with a small amount of cold water, and dried under vacuum at 70 °C. The crude product was dissolved and chromatographed with chloroform/methanol (97:3, v/v) on a column of neutral alumina (25 × 200 mm). The main product was dissolved in 10 mL of DMF, and 0.25 mL of methyl iodide was added. The mixture was stirred at 45 °C for 3 h and then concentrated to a few milliters. Water (50 mL) was added, and the solution was filtered. Sodium perchlorate (300 mg) was added to the filtrate, and the reaction mixture was left overnight at 4 °C. The precipitate was collected and dissolved again in water. A small amount of ion-exchange resin, Dowex 1X2-400, was used to accelerate dissolution. The solution was then charged on a column of Dowex 1X2-400 (200−400 mesh; chloride form; 10 × 200 mm), and the eluate was evaporated to dryness and dried in vacuo at 70 °C. Yield: 83 mg (37%). UV−vis (water, pH 7); 378 (52 200), 470 (93 400), 560 (13 300), 779 (2100).

(*meso*-Tetrakis(1-methyl-4-pyridinium)porphyrinato)manganese(III) Pentachloride (2). The same procedure was applied as for **1**. *meso*-Tetrakis(1-methyl-4-pyridinio)porphyrin (100 mg, 161 μmol; Alfa) yielded 61 mg of product. Yield: 33%. UV−vis (water, pH 7): 377 (41 300), 398 (41 400), 463 (106 100), 559 (10 700), 772 (1600).

(*meso*-Tetrakis(4-sulfonatophenyl)porphyrinato)manganese(III) (3). Preparation of H_2TPPS and metalation to Mn^{III}TPPSCl were achieved following the literature method[9] with modifications as described here. Tetrasodium *meso*-tetrakis(4-sulfonatophenyl)porphine dodecahydrate (150 mg, 121 μmol; Strem) and manganese(II) acetate tetrahydrate (400 mg, 1.63 μmol) were dissolved in 20 mL of water. The solution was heated to 85 °C for 3 h and then cooled to 20 °C. The reaction mixture was diluted with 120 mL of water to dissolve the precipitate, and the solution was passed through a column of Dowex 50WX8 using water as on eluent (60−170 mesh; 10 × 200 mm). The eluent was evaporated to dryness by a rotary evaporator and then dissolved in a small amount of methanol. The solution was charged on a column of Sephadex LH-20 (10 × 240 mm). A yellowish-brown impurity band was eluted first. The second, dark brown band was collected. Yield: 73 mg of a brown powder (49%). UV−vis (water, pH 7): 379 (58 400), 400 (59 400), 466 (99 100), 516 (7600), 564 (12 900), 596 (8900), 700 (1700), 778 (1900). MS (FAB$^-$) *m/z*: 985 ($[M - H]^-$).

(*meso*-Tetrakis(3-carbomethoxyphenyl)porphyrinato)manganese(III) Acetate. The literature method[9] was modified. In a 250-mL round-bottomed flask were placed 3-carboxybenzaldehyde (1.01 g, 6.53 mmol), pyrrole (0.46 mL, 6.4 mmol), manganese(II) acetate tetrahydrate (0.907 g, 3.70 mmol), and propionic acid (100 mL). The mixture was heated at reflux for 1 h and evaporated to dryness. The residue was dissolved in 100 mL of distilled CH_2Cl_2, and 75 mL of oxalyl chloride was added. The mixture was kept at 40 °C for 2 h. The solvent and the excess of oxalyl chloride were removed in vacuo. The residue was redissolved in 150 mL of distilled CH_2Cl_2, and 100 mL of methanol was added. The solution was stirred for 12 h at ambient temperature, and after evaporation of the solvent, the residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on a silica gel column ($\O = 5$ cm, $h = 40$ cm, CH_2Cl_2/CH_3OH, 96:4). The pure product was a green solid (430 mg, 0.42 mmol). Yield 26%. UV−vis (CH_2Cl_2) λ_{max} nm (ϵ M^{-1} cm^{-1}) 375 (48 600), 400 (38 750), 476 (91 700), 527 (4800), 582 (8100), 617 (8250), 764 (530).

(*meso*-Tetrakis(3-carboxyphenyl)porphyrinato)manganese(III) Chloride (4). In a 250-mL round-bottomed flask were placed (*meso*-tetrakis(3-carbomethoxyphenyl)porphinato)manganese(III) acetate (0.30 g, 0.29 mmol), potassium hydroxide (1.00 g, 17.8 mmol), water (10 mL), and methanol (100 mL). The mixture was refluxed for 3 h. The reaction mixture was acidified to pH 2 with HCl, and the precipitate was filtered off. The product was a dark-green solid (0.30 g, 0.29 mmol, quantitative yield). UV−vis (H_2O, pH 7) λ_{max} nm (ϵ M^{-1} cm^{-1}): 380 (52 800), 401 (52 000), 420 (36 000), 468 (83 300), 514 (7000), 565 (12 100), 599 (8700), 780 (1600), 813 (1500).

Spectrophotometric Measurements. A Perkin-Elmer Lambda 16 UV−vis spectrophotometer was used for measuring electronic absorption spectra. To prepare aqueous solutions, 10 mM phosphate buffer (pH 7.0), 10 mM borate buffer (pH 9.0), or a 10 mM sodium hydroxide solution (pH 12.0) was used. Quartz cuvettes (10 n/mm) were used for acid−base titrations. In spectrophotometric titrations, dilution was less than 2%.

Electrochemical Measurements. All aqueous solutions used for electrochemistry were prepared from triply distilled water. Preparation of all solutions was carried out under an N_2 atmosphere. Dilute HCl and NaOH were used to adjust the pH. The errors in pH values were within ±0.02 pH units. All reported potentials are with respect to the Ag/AgCl reference electrode. The ionic strength was maintained at 0.2 M with KCl. Cyclic voltammetric measurements were carried out with a three-electrode potentiostat (Versastat potentiostat, EG&G, Princeton, NJ). A glassy-carbon (surface: 3.14 mm^2), a gold (surface: 3.14 mm^2), or a platinum electrode (surface: 3.14 mm^2) was employed as the working electrode. An Ag/AgCl electrode (Sensortechnik, Meinsberg, GmbH) with saturated KCl served as a reference. The counter electrode was made of platinum. In the spectroelectrochemical studies, a standard three-electrode system was used together with a Bruker E 130 M potentiostat and a high-impedance millivoltmeter (Minisis 6000, Tacussel). Measurements were carried out in H_2O at pH 12 (0.01 M NaOH) with 0.2 M KCl using a Pt grid (100 mesh) OTTLE (optically transparent thin-layer electrode) working electrode. Spectra were recorded on a Hewlett-Packard 8452 A diode array spectrophotometer. The thin-layer spectrochemical cell has been previously described by Bernard et al.[9,10]

Measurement of Dissolved Dioxygen during Electrooxidation of Heterotrimers. Quantitative measurements of the dioxygen formed upon oxidation of the manganese porphyrin heterotrimers were performed at 20 °C with a dissolved-oxygen electrode (Oxi-Meter OXI 96, WTW, GmbH). In a typical experiment, tridistilled deoxygenated water (40 mL), with 50 μL of tetraethylammonium hydroxide (TEAOH, 40%) and tetraethylammonium perchlorate (TEAP, 0.2 M) as the supporting electrolyte at pH 12, was placed in a four-necked flask (100 mL). One neck contained the oxygen electrode, one the working electrode (Pt grid), one the counter electrode (Pt), and one the reference electrode (Ag/AgCl). Back ground oxygen evolution in the absence of heterotrimers was also observed upon electrooxidation above 0.6 V vs Ag/AgCl. All of the measurements were repeated several times in the presence and in the absence of the catalyst. Dioxygen formed when the catalyst was absent was subtracted from the values obtained with the catalyst.

Results

(β-Tetraethyl-β-tetrakis(1-methyl-4-pyridinium)porphyrinato)manganese(III) chloride **1** was synthesized as a mixture of four regioisomers **I**−**IV**.[6,7] Isomers **I** and **II** were removed by chromatography on silica gel. We applied only the remaining mixture of isomers **III** and **IV** (Chart 1). This mixture is soluble in water at pH values from 1 to 12 and up to concentrations of about 1×10^{-2} M. (*meso*-Tetrakis(1-methyl-4-pyridinium)porphyrinato)manganese(III) chloride **2** and (*meso*-tetrakis(4-sulfonatophenyl) porphyrinato)manganese(III) chloride **3** were readily prepared by metalation of commercial porphyrins and are soluble in water up to concentrations of 10^{-2} M. (*meso*-Tetrakis(3-carboxyphenyl)porphyrinato)manganese(III)

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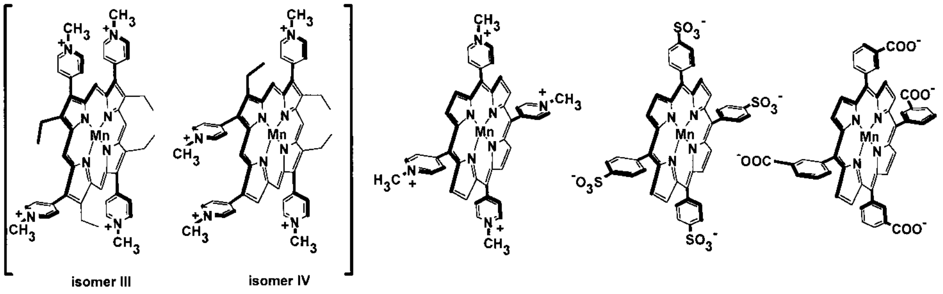
Chart 1



1 2 3 4

Table 1. pK_a Values of Manganese Porphyrins

compound	pK_{a1}	pK_{a2}	
1		10.6^a ± 0.1	10.6^b ± 0.2
2	8.0^c	10.6^a ± 0.1	10.6^b ± 0.2
3	8.6^c	12.3^a ± 0.1	12.0^b ± 0.4
4		11.9^a ± 0.1	11.9^b ± 0.3

[a] By spectrophotometric titration. [b] By electrochemical titration. [c] By spectrophotometric titration. See: ref 9,

chloride **4** is soluble in water only above pH 5.5. All aqueous solutions were stable for days without any precipitation or bleaching.

The UV–vis spectra of manganese(III) porphyrinates dramatically change with pH because the manganese axial ligands influence manganese porphyrin d(π) interactions. At high pH, proton-coordinated water molecules dissociate, and the charge of the metal center changes without any redox reaction taking place. Because manganese(III) porphyrins have two water molecules as axial ligands, one expects two such dissociation steps.[10,15] Only one distinct change in absorption spectra has, however, been described so far at pH 10–12.[11] It should also be noted that the half-wave potentials for Mn(III) porphyrins are independent of the pH in the range of 5–11.[11b,c] Thus, we have determined only the second pK_a by spectrophotometric and electrochemical titration and calculated the acid dissociation of manganese(III) porphyrin from Nernst–Clark plots. pK_a values for **1**–**4** are listed in Table 1. At pH 12, where most experiments have been performed, we therefore dealt with the [Mn(III)(OH)$_2$] anion whereas at pH 9–10 the electroneutral monohydroxide prevailed. At pH 7, the spectrum of a mixture of **1** and **3** was equal to the sum of the individual compounds (not shown), but it was quite different at pH 9 and especially at pH 12 (Figure 1). Extensive line broadening, loss of absorption intensity, and a small blueshift were observed at high pH and were totally reversed upon going to pH 7.

Job plots of titrations of cationic and anionic porphyrins at pH 12 (Figure 2) indicated the initial formation of a **1**–**3**–**1** (cation–anion–cation) trimer, with subsequent appearance of the **3**–**1** heterodimer (Figure 3). Reverse titration of the anionic porphyrin **3** with the cationic porphyrin **1** yielded first a dimer, then a trimer (Scheme 1).

The pairing of β-pyridinium tetracation **1** and tetracarboxylate **4** yielded similar results. Solutions of heterodimers or -trimers were stable at concentrations of less than 10^{-4} M. In 10^{-3} M solutions, precipitates formed after several hours. Combinations of meso-substituted porphyrins **2** and **3** (or **2** and **4**) were much less soluble and shorter-lived in water. The spectrum of a solution containing **2** and **3** (or **2** and **4**) is only slightly different from the sum of the spectra observed for the individual components for **2** and **3** (or **2** and **4**) at pH 12. Small crystals formed slowly, even from very dilute solutions. This indicates that alternating heteropolymers were formed rather than the heterodimers.[4]

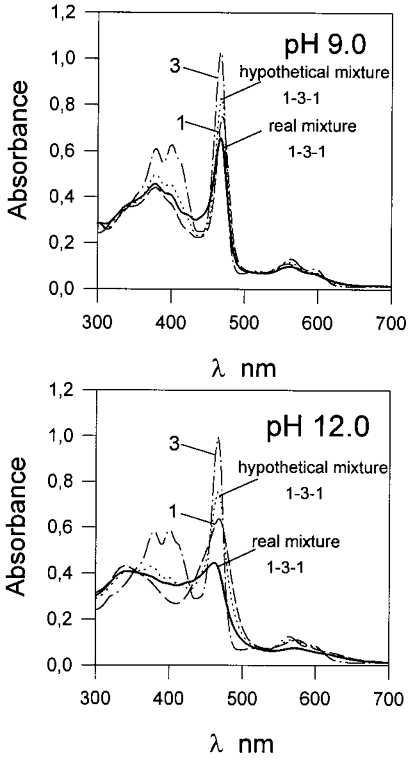


Figure 1. Electronic absorption spectroscopic changes upon mixing cationic Mn(III) porphyrin **1** with anionic Mn(III) porphyrins **3**. The spectra are shown for 2:1 mixtures of **1** and **3** at pH 9 (top) and **1** and **3** at pH 12 (bottom). The total concentration of the porphyrins was kept at 1×10^{-5} mol dm^{-3}.

The Mn(III) porphyrinate dimer **1**–**3** was also titrated with the free base porphyrin mixture **1**. The heterotrimer with two redox-active manganese porphyrins and one free base was obtained. This trimer showed neither any fluorescence nor phosphorescence at room temperature. The distance between the "antenna" free base porphyrin and the manganese porphyrinates is obviously too short to allow fluorescence. Further experiments with cationic spacers on the pyridinium rings of the free base porphyrin have been undertaken to overcome this quenching effect.

Electrochemistry and Spectroelectrochemistry of Monomers, Heterodimers, and Heterotrimers. All redox potentials, E, are approximated in the following by $E^{\circ\prime} = (E_p^a + E_p^a)/2$ (in

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(11) (a) Balasubramanian, P. N.; Schmidt, E. S.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 7865. (b) Harriman, A. *J. Chem. Soc., Dalton Trans.* **1984**, 141. (c) Balahura, R. J.; Kirby, R. A. *Inorg. Chem.* **1994**, *33*, 1021.

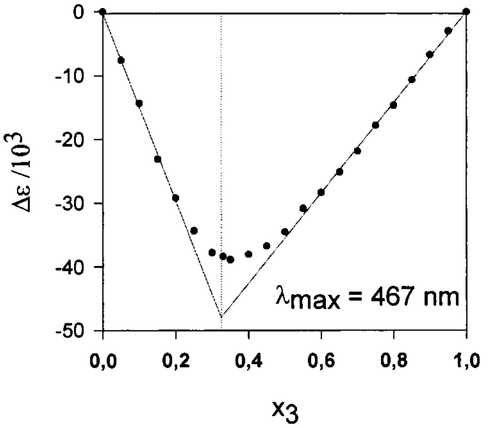

Figure 2. Job plot of the spectroscopic changes against molar ratio of **3** for the titration of **1** with **3**.

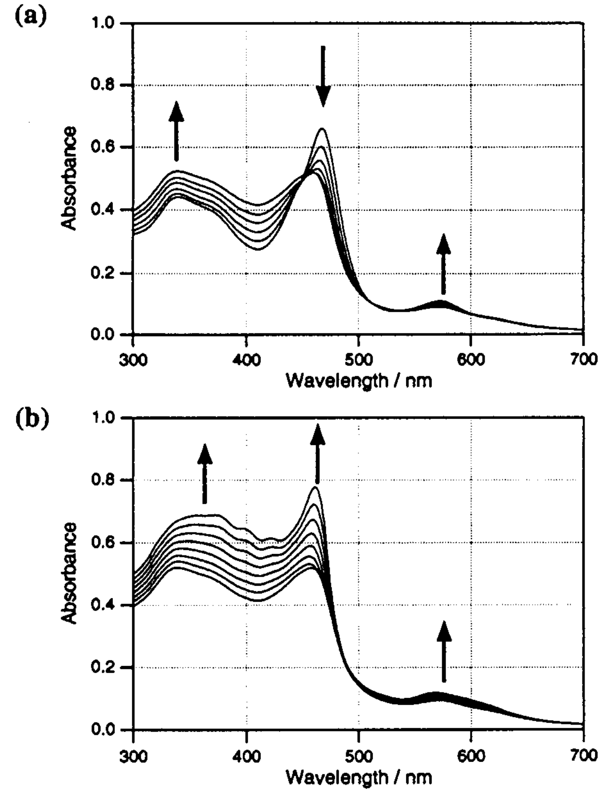

Figure 3. Change in electronic absorption spectra upon titration of cationic Mn(III) porphyrin **1** with anionic porphyrin **3** at pH 12. The initial concentration of **1** was 1 × 10^{-4} mol dm^{-3}. (a) Start: 100% the tetracation **1**. End: ratio of **1**−**3** = 2:1 corresponding to the **1**−**3**−**1** heterotrimers. (b) Conversion to the **1**−**3** dimer by addition of an excess of porphyrin **3**.

Scheme 1

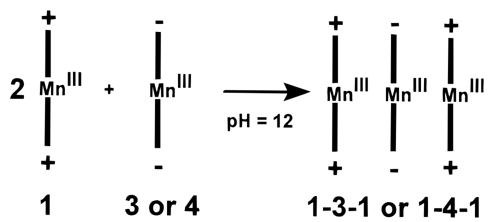

Table 2. Electrochemical Data of the Studied Porphyrins, Heterodimers and Heterotrimers[a]

compound	ring oxidation of porphyrin	$Mn^{III} \rightarrow Mn^{IV}$	$Mn^{III} \rightarrow Mn^{II}$	pyridinium reduction
1		0.18	−0.17 -0.11^{c}	$-0.74^{4e,b}$
2		0.20	−0.18 -0.13^{c}	$-0.68^{4e,b}$ $-0.60^{irr,4e,c}$
3			-0.41^{a} -0.39^{c}	
4	$0.69^{irr,b}$		-0.45^{b} -0.44^{c}	
1−**3**−**1**		$0.30^{irr,3e}$	$-0.35^{irr,3e}$	$-0.77^{irr,8e}$
3−**2**		0.25^{2e}	-0.20^{2e}	-0.68^{4e}
1−**4**−**1**		0.23^{3e}	-0.15^{3e}	$-0.87^{irr,8e}$
4−**2**		0.25^{2e}	-0.18^{2e}	

[a] All redox potentials $E°$, approximated by $(E^{a} + E^{c})/2$ for the reversible steps, are given in volts vs Ag/AgCl as obtained from cyclic voltammetry ($v = 50$ mV s^{-1}) in H_2O, KCl (0.2 M), and pH 12 (NaOH 0.01 M). The number of exchanged electrons for each system was determined by a comparison between the limiting currents of the different waves characterizing a given system. A glassy-carbon working electrode (surface area: 3.14 mm^2) was used, except were noted. [b] Working platinum electrode (surface area: 3.14 mm^2). [c] Potentials measured at pH 7. [d] Working gold electrode (surface area: 3.14 mm^2).

volts) vs Ag/AgCl. The number of exchanged electrons for each system was determined by comparison between the limiting currents of the different cyclic voltammetry (CV) waves characterizing a given system. The electrochemical data are summarized in Table 2, and typical cyclic voltammograms are presented in Figure 4. The assignment of the site undergoing the electron transfers was based on spectroelectrochemical studies in H_2O at pH 12.

CV's of tetrapyridinium porphyrins **1** and **2** at pH 7 showed only Mn(III) → Mn(II) reduction steps at −0.11 and −0.13 V. At pH 12, reversible one-electron reduction and oxidation[12,13] reactions became detectable (Figure 4a). The tetrasulfonato porphyrin **3** and the tetracarboxylato porphyrin **4** at pH 12 also show one reductive step at −0.41 and −0.45 V, respectively, using Pt electrodes (Figure 4b). These ill-defined waves were also detectable with Au and glassy-carbon electrodes. An irreversible 690-mV wave (only for **4**) on the Pt electrode (not shown) indicated porphyrin oxidation; the increasingly electron-rich environment provided by the carboxylato substituents obviously favors the generation of a porphyrin cation radical.

For tetrasulfonato porphyrin **3** at the somewhat higher pH of 12.60, an additional, completely irreversible, one-electron wave at −75 mV vs Ag/AgCl was observed and may correspond to the electrogeneration of the μ-oxo Mn(IV) porphyrin dimer[3c,16] either from the anionic dihydroxide $\{2[HO{-}Mn^{III}TPPS{-}OH]^{-} \rightarrow [HO{-}Mn^{IV}TPPS{-}O{-}Mn^{IV}TPPS{-}OH] + H_2O + 2e\}$ or the μ-oxo dimer of Mn(III). A similar wave was also observed with the tetracarboxylato porphyrin **4**.

When the glassy-carbon electrode was used in H_2O at a pH of 12, the meso heterodimers **3**−**2** and **4**−**2** showed two reversible two-electron redox waves for the Mn^{III}/Mn^{II} and Mn^{IV}/Mn^{III} couples. The redox potentials are close to those of the *meso*-pyridiniumporphyrin **2**. A cathodic shift (0−20 mV) for the reduction and a anodic shift (50 mV) for the oxidation were observed. No wave was observed in the range from −0.30 to

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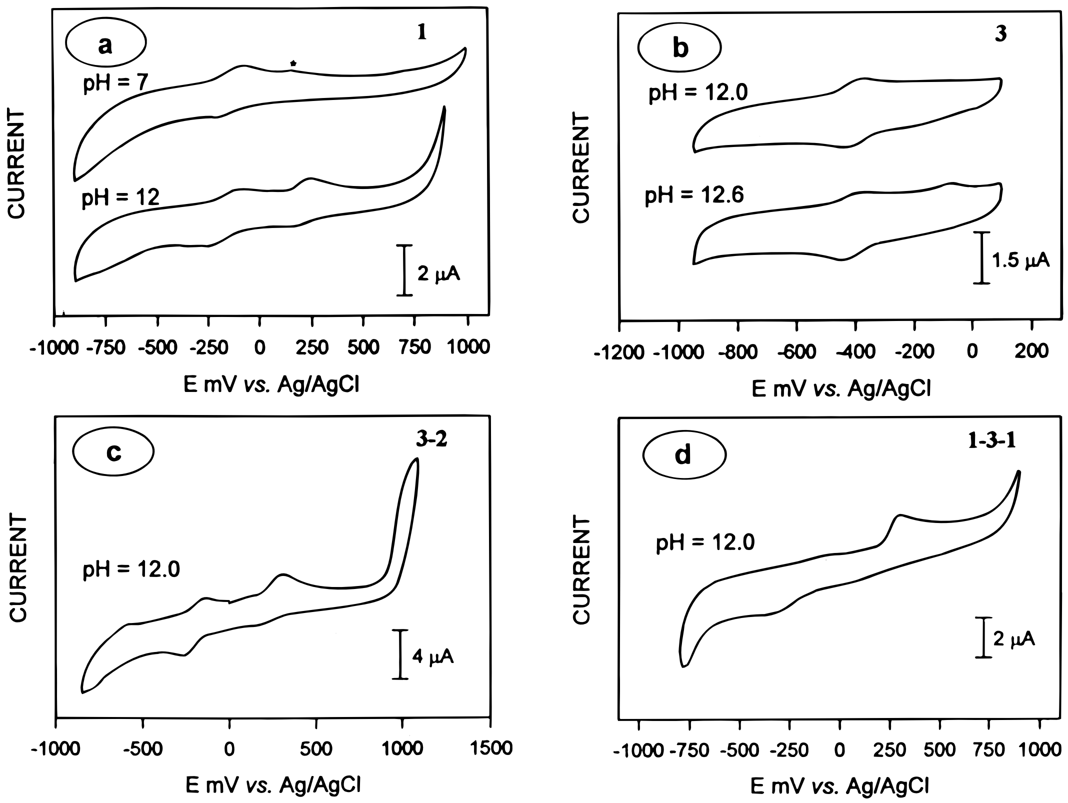

Figure 4. Cyclic voltammograms: (a) At pH 7.0 and 12.0 for manganese(III) porphyrinate **1** (working electrode: glassy-carbon electrode). **2** gives similar CV's. (b) At pH 12.0 and 12.6 for **3** (working electrode: Au). **4** gives similar CV's. (c) At pH 12.0 for heterodimer **3**−**2** (working electrode: glassy-carbon electrode). (d) At pH 12.0 for the resulting heterotrimer **1**−**3**−**1** (working electrode: glassy-carbon electrode). Scan rate: $v = 50$ mV s^{-1}). The concentration of the porphyrin was kept at 1×10^{-4} M, except for cyclic voltammogram c (2×10^{-4} M).

Table 3. Molar Extinction Coefficients for Manganese Porphyrins

compound	oxidation no. of Mn	pH	Soret band λ_{max} (nm)	$\epsilon \times 10^3$ dm^3 mol^{-1} cm^{-1}	ϵ(V)/ϵ(VI)[a]
1	II	12	462	66	
	III	7	470	93	1.79
		12	468	69	
	IV	12	430	74	
2	II	7	441[a]	133[a]	
		12	446	58	
	III	7	463	102	2.45
		12	462	68	
	IV	12	426	62	
3	II	7	436[a]	342[a]	
		12	434	304	
	III	7	466	99	1.67
		12	464	95	
	IV ↔ P$^{•+}$	12	420	62	
4	II	12	432	318	
	III	7	468	83	1.58
		12	466	59	
	IV ↔ P$^{•+}$	12	422	103	

[a] The value reported by Harriman and Porter (ref 14). [b] The ratio of the molar extinction coefficient for Band V to that for Band VI.

−0.65 V vs Ag/AgCl, where the anionic porphyrin monomers **3** and **4** are reduced (Figure 4c).

At pH 12, the *β*-meso *β* heterotrimer **1**−**3**−**1** did not produce the expected three-electron reversible waves, but it did produce two three-electron irreversible processes at −0.35 and +0.30 V (Figure 4d). The heterotrimer **1**−**3**−**1** was oxidized at a constant potential of 0.5 V. Well-defined isosbestic points indicated a clean conversion of all three manganese(III) centers to manganese(IV) ions.

Spectroelectrochemical investigation of the oxidation of *β*-tetrapyridinium porphyrin **1** or *meso*-tetrapyridinium porphyrin **2** at a constant potential of 0.5 V vs Ag/AgCl, on the other hand, showed the formation of a 430-nm Soret band typical of the manganoyl(IV) porphyrinate. Isosbestic points were not observed in the reduction sequence but occurred in the oxidation reaction. These observations are consistent with those of Harriman for the porphyrin **2**.[14]

At pH 12 and at a controlled potential of −0.5 V vs Ag/AgCl, the sulfonate **3** gave two sharp isosbestic points and an extraordinary increase of the Soret band intensity by a factor of 3 (see Table 3). Not only is the Soret band of the Mn(III) complex broad and split, but also the Q bands are extremely broadened, indicating exceptionally strong $\pi \rightarrow d(\pi)$ interactions. Oxidation of **3** at a higher potential of 0.9 V vs Ag/AgCl gave another product with even more broadened visible bands, probably indicating a porphyrin radical cation. At pH 12, no oxidation step was observed before oxidation of the gold electrode occured or the anodic solvent-accessible potential limit of the Pt or glassy-carbon electrode was reached. Spectroelectrochemical studies using a Pt grid electrode showed radical formation at a controlled potential of 0.9 V vs Ag/AgCl.

When the carboxylate **4** was electrolyzed at −0.5 V vs Ag/AgCl, a blueshift of 34 nm for the Soret band and 4−8 nm for the Q band occurred (Figure 5), indicating manganese(II) complex formation in a one-electron reaction. **4** was also cleanly oxidized at +0.5 V to the manganoyl(IV) porphyrinate as evidenced by the 422-nm Soret band.[14] Six sharp isosbestic points were observed (Figure 5).

Spectroelectrochemical studies of the meso heterodimers **3**−**2** and **4**−**2** at a controlled potential of 0.5 V vs Ag/AgCl and pH 12 showed oxidation of Mn(III) to O=Mn(IV) porphyrins which was fully reversible (Figure 6). Electroreduction of heterodimers at the controlled potential of −0.5 V vs Ag/AgCl produced Mn^{II}

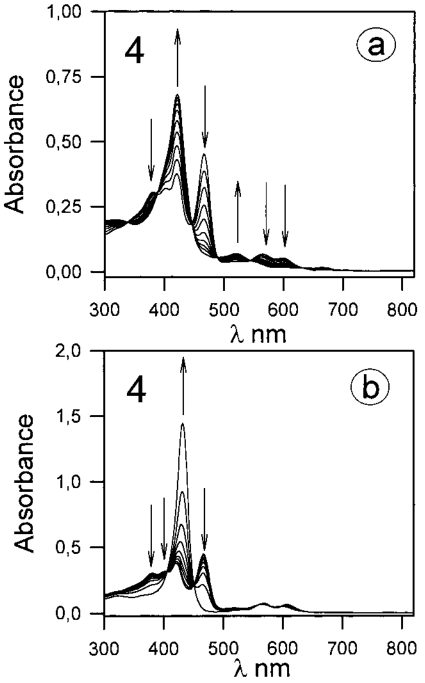

Figure 5. UV−visible absorption spectra recorded during (a) the oxidation of the manganese tetracarboxylate porphyrin **4** at +0.5 V vs Ag/AgCl (pH 12) and (b) the reduction of **4** ($Mn^{III} \rightarrow Mn^{II}$) at −0.5 V vs Ag/AgCl (pH 12.)

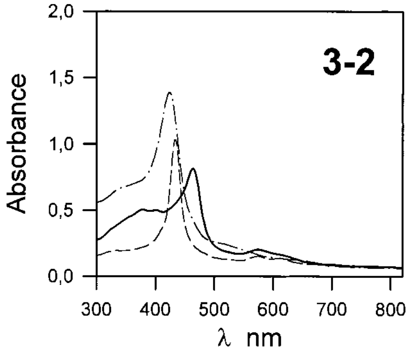

Figure 6. UV−vis absorption spectra recorded during the oxidation of the heterodimer **3**−**2** at +0.5 V and its reduction **2** at −0.5 V vs Ag/AgCl (pH 12): Mn(III) (—), Mn(IV) (- · -), Mn(II) (- - -).

heterodimers and was fully reversed at 0 V. No isosbestic points were, however, apparent. Heterodimer **4**−**2** yielded similar results (Figure 6).

Manganese(III) and manganese(IV) heterotrimers **1**−**3**−**1** and **1**−**4**−**1** are characterized by a practically complete loss of Q bands. Only an extremely broad absorption ranging from about 550 to 700 nm remained (Figure 7a). Electrochemical reduction of the Mn(III) heterotrimer **1**−**3**−**1** to Mn(II) did very surprisingly not occur at all on the Pt working electrode. It was, however, possible to obtain the Mn(II) heterotrimer reduction with dithionite at pH 12 in quantitative yield (Figure 7b).

A similar redox and spectroscopic behavior was observed for the second β-meso β heterotrimer **1**−**4**−**1**. Although cyclic voltammetry exhibited three-electron quasi-reversible waves for both reduction and oxidation processes and electrochemical oxidation also occurred quantitatively, electrochemical reduction could not be detected in the UV−vis spectra. Chemical reduction with 1 equiv of dithionite for each manganese(III) produced, however, the Mn(II) trimer in quantitative yield as indicated by the Soret band at 426 nm.

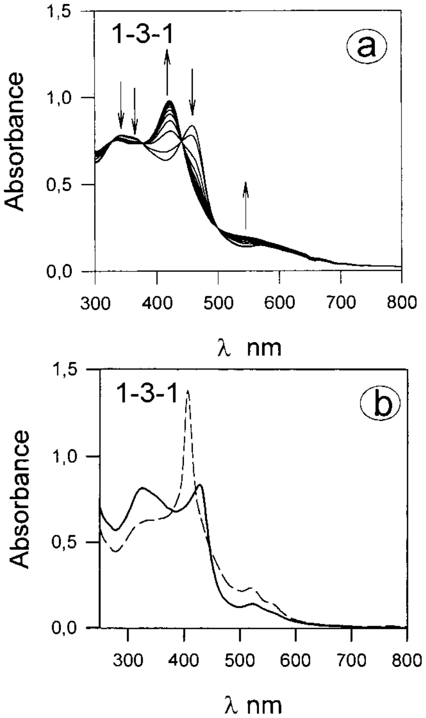

Figure 7. UV−vis absorption spectra recorded (a) during the oxidation of heterotrimer **1**−**3**−**1** at +0.5 V vs Ag/AgCl (pH 12) and (b) after chemical reduction of Mn(III) in heterotrimer **1**−**3**−**1** (pH 12).

Dioxygen Evolution. The capability of the heterotrimers **1**−**3**−**1** and **1**−**4**−**1** to catalyze the electrochemical oxidation of H_2O at pH 12 was investigated in the potential range between 0.6 and 2.0 V. At 2.0 V vs Ag/AgCl and after Mn(III) was oxidized to O=Mn(IV), dioxygen evolution occurred at a constant rate for about 4 min. Thereafter, the solution decolorized, and the rate of oxygen evolution soon decreased to 0 (Figure 8).

One heterotrimer molecule produced about 7.5 molecules of dioxygen. At 1.2 V, oxygen evolution was first-order with respect to the complex and had a maximum rate = 1.190 mol of O_2 (mol of cat.)$^{-1}$ min^{-1}. At this potential, no degradation of the porphyrins was observed, but the turnover number decreased to 4.5. When the heterotrimers **1**−**3**−**1** and **1**−**4**−**1** were oxidized at 0.6 V vs Ag/AgCl, the rate of oxygen evolution dropped to 0.032 and 0.045 mol of O_2 (mol of cat.)$^{-1}$ min^{-1}, respectively. Simple cationic Mn(IV) porphyrins **1** and **2** which assemble to form homodimers at pH 12 were, however, as active in oxygen evolution as the heterotrimers. No oxygen evolution was observed for anionic porphyrins **3** or **4**. The meso heterodimers **3**−**2** and **4**−**2** showed intermediate activity (Table 4). By far the most efficient system was supplied by the β-meso heterodimer pairs **1**−**3** and **1**−**4**. Turnover numbers were about twice as high as those with homodimers.

Discussion

The electronic absorption spectra of Mn(III) porphyrins show two bands with weak intensities in the near-infrared region (bands I and II), two bands in the visible region corresponding to the Q(0,0) and Q(1,0) bands (bands III and IV) which are generally found in metal porphyrins, and two bands with strong intensities at around 450 and 350 nm (bands V and VI). Band VI has been ascribed to ring-to-metal charge-transfer (CT)

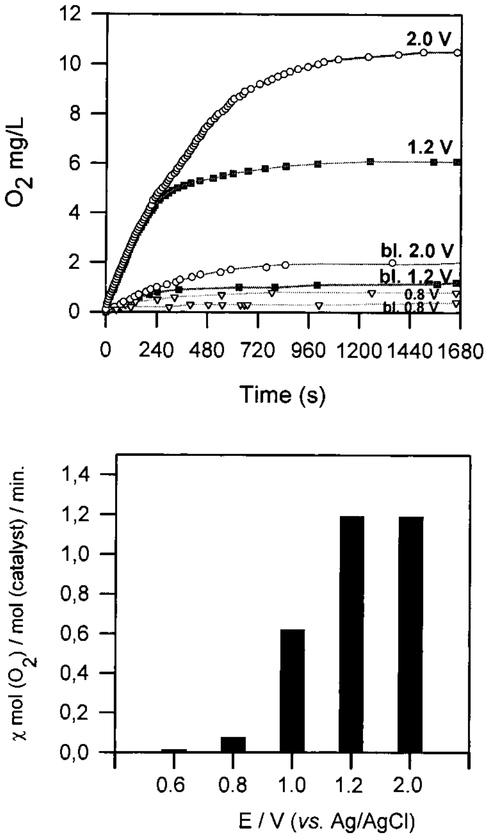

Figure 8. Top: plot of the dioxygen formed during oxidation of heterotrimers **1**−**3**−**1** ($c = 3.4 \times 10^{-5}$ M) at 0.8, 1.2, and 2.0 V vs Ag/AgCl with 50 μL of TEAOH (40%) −TEAP (0.2 M) as the supporting electrolyte (pH 12) versus time (s). Bottom: rate of oxygen evolution for **1**−**3**−**1** at different applied potentials.

Table 4. Maximum Rate of Oxygen Evolution[a] Cycle Number[b] Measured at pH 12 and Different Potentials

compound	0.6 V	1.0 V	1.2 V	2.0 V
1−**1**[c]	0.068 (0.03)	1.362 (3.8)	2.452 (4.0)	2.472 (6.6)
1−**3**	0.036 (0.05)	0.750 (6.4)	1.080 (6.4)	2.043 (14.0)
1−**3**−**1**	0.032 (0.04)	0.618 (4.1)	1.190 (4.5)	1.190 (7.5)
1−**4**	0.031 (0.04)	0.540 (6.0)	1.562 (6.8)	1.562 (14.2)
1−**4**−**1**	0.045 (0.05)	0.688 (4.2)	1.203 (4.7)	1.210 (7.2)
2−**2**[c]	0.034 (0.02)	0.742 (2.5)	1.241 (2.7)	1.270 (7.2)
2−**3**	0.042 (0.03)	1.008 (3.9)	1.874 (4.7)	1.984 (9.4)
2−**4**	0.071 (0.04)	1.411 (3.7)	2.339 (4.5)	2.534 (9.4)
3				0.035 (0.03)
4				0.024 (0.02)

[a] Maximum rate of oxygen evolution = mol of O_2 (mol of cat.)$^{-1}$ min^{-1}. [b] Maximum cycle number = (maximum O_2)/(cat. formed). Shown in parentheses. [c] Presumably as the homodimer at pH 12.

transition, $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(d_\pi)$.[17,18] The CT transition is allowed because the $e_g(d_\pi)$ orbital mixes with the $e_g(\pi^*)$ orbital. The mixing is accompanied by a decrease in the intensity of band V, $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(\pi^*)$. For (*meso*-tetraphenylporphyrinato)manganese(III) chloride (Mn^{III}TPPCl), the molar extinction coefficient (ϵ) for band V is about 8×10^4 M^{-1} cm^{-1}, and the ratio of the extinction coefficients of bands V and VI is about 2.[19] The values of these parameters and other characteristics of the electronic absorption spectra for Mn(III) porphyrins **1**−**4** (Table 3) are similar to those of Mn^{III}TPPCl. The substituents on the periphery of the porphyrin ring obviously hardly effect the electronic structure of the Mn(III) porphyrins.

The spectra of Mn(II) and Mn(IV) porphyrinates obtained by spectroelectrochemical studies show large differences in the extinction coefficients of the cationic porphyrins (**1** and **2**) and the anionic porphyrins (**3** and **4**). The much smaller extinction coefficient for the cationic Mn(II) porphyrins can be explained as either aggregation of the cations or electron donation from Mn(II) to the β-pyridinium substituents. The latter effect should, however, lead to strong changes in the Q bands (e.g., to a chlorine-like spectrum), but this is not observed. We therefore propose aggregation as a major source of Soret band flattening.

Extreme broadening of the Soret band is only observed for the cationic porphyrins; the half-width bands observed for **1** and **2** are 80 and 55 nm whereas for **3** and **4** values of about 22 nm were found. At pH 12, the central Mn(II) ion is coordinated by hydroxide and therefore produces a negative charge. In the case of the cationic porphyrin ligands, this charge is partly neutralized and aggregation occurs whereas charge repulsion prevents the aggregation of anionic Mn(II) porphyrins. At pH 7, Mn(III) porphyrins have an extra positive charge at the center of the porphyrin ring, at pH 9, the charge is neutralized, and at pH 12, we again assume a negative charge. The failure in making the heterodimers and -trimers at pH 7 can then be attributed to the repulsion between positive charges in the porphyrin centers. Aggregation to dimers does not lead to dramatic changes in the spectra. Extensive line broadening is the most obvious effect.

At pH values above the second pK_a of the complexes, Mn(III) porphyrins produce μ-oxo homo-[20] or heterodimers. The meso-substituted, anionic Mn(III) porphyrins **3** and **4** form dimers and trimers with β-substituted porphyrins whereas the meso-substituted porphyrin **2** also polymerizes.[4] Moreover, while meso-substituted porphyrins can stack only in a staggered conformation, the β-substituted porphyrin lies on a meso-substituted one in an eclipsed conformation. Because a typical Mn(III) porphyrinate heterodimer has four positive and six negative charges at pH 12, a typical heterotrimer has eight positive charges and seven negative charges. The more effective cancellation of charge may then be responsible for the observed preference of the trimer.

For the monomeric anionic porphyrins **3** and **4**, the reduction potentials of the Mn(III) → Mn(II) conversion are all close to −410 or −450 mV, and for the cationic porphyrins **1** and **2**, values are close to −170 and −180 mV, respectively. At pH 12, reduction remains easy, even in the case of two axial hydroxide ligands. The most interesting oxidation to Mn(IV) porphyrins or manganese(III) porphyrin cation radicals, which should lead to oxygen formation, also occurs readily. Bulk electrolysis of heterodimers **3**−**2** and **4**−**2** showed that at pH 12 they can be reduced from Mn(III) to Mn(II) and oxidized from Mn(III) to O=Mn(IV). Spectroelectrochemistry of the heterotrimers **1**−**3**−**1** and **1**−**4**−**1**, on the other hand, revealed only clean conversions of manganese(III) to manganese(IV) but electroreduction even at a potential of −0.65 V did, very surprisingly, not occur at all, although cyclic voltammograms showed an irreversible cathodic process at −0.35 V for **1**−**3**−**1** (Figure 4c). Nevertheless, chemical reduction occurred readily with dithionite. We rationalize this observation of electrode inertness with the assumption that the central manganese(III) ions can only be reduced by direct electron transfer from the

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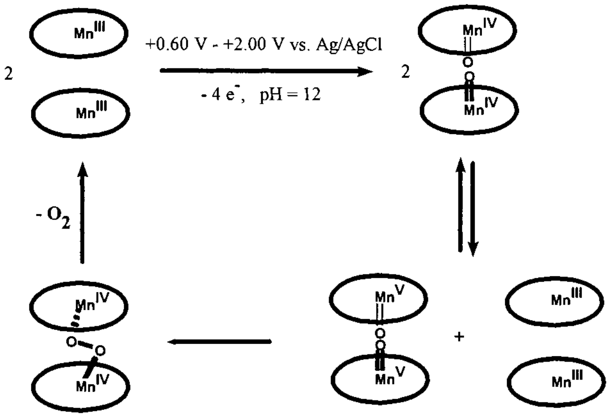

Figure 9. Proposed mechanism of dioxygen evolution during electrooxidation of heterodimer of manganese(III) porphyrins.

electrode to manganese. This transfer is inhibited by the terminal hydroxide counterions, but it can occur if dithionite ions replace them. The loosely bound and ill-defined oligomers of *meso*-tetrapyridinium[4] and *meso*-tetraphenylsulfonato or -carboxylato porphyrins, **2** and **3** or **2** and **4**, on the other hand, not only could be oxidized to Mn(IV) heterodimers at +0.5 V but also are reduced at a potential of −0.5 V.

The first structurally characterized and truly catalytic manganese porphyrinate oxidation catalyst for water oxidation consisted of a covalent *o*-phenylene-bridged dimer.[8] It worked at a potential above 1.2 V (vs Ag/Ag$^+$) in a mixed CH_3CN/CH_3OH (95:5) solvent containing *n*-Bu_4NOH/*n*-Bu_4NClO_4 as the supporting electrolyte. The measured number of the reaction cycles for the most active species was 9.2, and the rate of dioxygen evolution was first-order [maximum rate: 0.110 mol of O_2 (mol of cat.)$^{-1}$ min^{-1} at 2.0 V] with a four-electron mechanism. For the heterotrimers (**1**−**3**−**1** and **1**−**4**−**1**), heterodimers (**3**−**2** and **4**−**2**), and homodimers (**1**−**1** and **2**-**2**), the organic solvent mixture was replaced by water at pH 12, and its electrochemical oxidation was achieved with a maximum cycle number between 6.6 and 9.4. We propose Mn(V)═O porphyrinates as intermediates in the reaction[3a−c,8] with direct coupling of the neighboring manganoyl−oxo groups, leading to a $Mn^{IV}-O-O-Mn^{IV}$ complex;[21] followed by O_2 release and recovery of the starting Mn(III) complex (Figure 9).

β-Mesoheterodimers show, in general, the fastest rates of oxygen evolution and the largest turnover numbers (Table 4). Trimers are less efficient. We propose that the manganese−manganese distance is optimal in the dimer to form oxygen bridges and that this distance grows upon addition of an extra porphyrin because the charge density is diminished.

Another possible pathway is to add water to an Mn═O group and subsequently to oxidize the resulting peroxo intermediate.

Conclusion

The most important question of whether noncovalent porphyrin heterodimers survive changes of redox states of central metal ions and, consequently, changes of axial ligands has been answered positively, provided the conditions are right. In the case of manganese porphyrins, this means high pH. At low pH, precipitation and dissociation reactions could not be avoided. High pH also proved to be optimal for the catalytic formation of dioxygen.

It has not been possible to produce multivalent manganese porphyrinate trimers. Only three-electron oxidations and reductions were observed in spectroelectrochemistry, which indicates strong electronic coupling of the three monomer units.

To be useful for photochemical oxygen evolution, the coupling with a photoactive porphyrin is mandatory. This has not been achieved so far because even manganese(III) ions quench the fluorescence of the free base porphyrins. Experiments with other A−B−C heterotrimers in which a manganese porphyrinate dimer is coupled with another free base or main group metalloporphyrin are currently under investigation. Spacers are applied which keep the photoactive components at a distance of ≥8 Å. If successful, the trimers introduced here may produce oxygen in light at high pH and may be coupled in a light-driven battery with ruthenium complexes producing hydrogen at low pH.

Acknowledgment. This work was supported by the European TMR research network Artificial Photosynthesis for Energy Production (Mn−Ru chemistry, Contract CT 96-0031), by a Humboldt fellowship, and the Deutsche Forschungsgemeinschaft (SFB 312 and SFB 348). We warmly thank Prof. A. Giraudeau, Dr. J.-P. Gisselbrecht, and Prof. M. Gross, Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Université Louis Pasteur, Strasbourg, France, for support concerning the electrochemical studies. We also thank Dr. U. Siggel, Technische Universität Berlin, for helpful discussion on the results.

Supporting Information Available: Complete spectroelectrochemistry studies of porphyrin monomers **1**−**3** and heterodimer **2**−**3**, as well as Job plots of **1**−**4**, and spectroscopic changes for titration of **3** with **1** and for the mixture **1**−**4** (8 pages). Ordering information is given on any current masthead page.

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