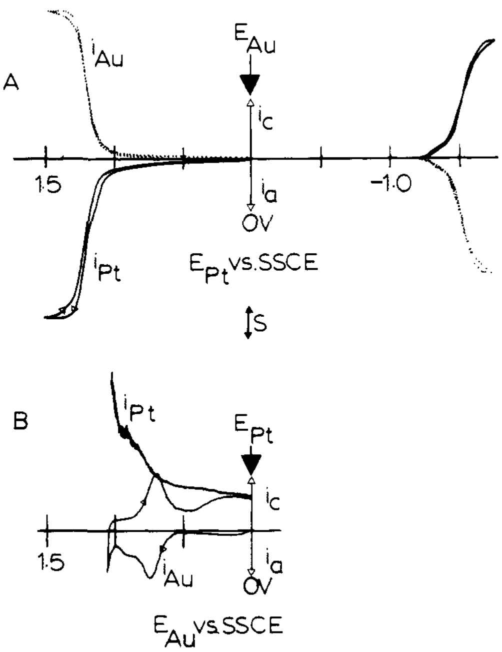

Figure 8. Four-electrode cyclic voltammetry of a bilayer sandwich electrode Pt/poly[Ru(bpy)$_2$(vpy)$_2$]$^{2+}$/poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$/Au with $\Gamma_{Ru} = 1.0 \times 10^{-8}$ and $\Gamma_{Os} = 9.4 \times 10^{-8}$ mol/cm^2. Curve A: $E_{Au} = 0$ V vs. SSCE and E_{Pt} scanned at 20 mV/s, $S = 5$ and 250 μA for positive and negative E_{Pt}, respectively. Curve B: $E_{Pt} = 0$ V vs. SSCE and E_{Au} scanned at 20 mV/s, $S = 5.0$ μA for i_{Au} and 0.25 μA for i_{Pt}, 0.1 M Et_4NClO_4/CH_3CN.

Ru(II) state, not a mixed-valent state and so is an insulator. At potentials near 1.22 V the ruthenium polymer conducts and so the osmium polymer is oxidized.

We have prepared a bilayer electrode sandwich of these two polymers to illustrate the rectifying behavior of the polymer film/film junction, with results shown in Figure 8. For $E_{Au} = 0$ V vs. SSCE, the redox conduction waves have a similar appearance to those obtained for a sandwich using a film of a single polymer. The redox conductions due to the M(II/I) and M(II/0) mixed-valent states (Schemes II and III) occur with similar magnitude ($i_L = 700$ μA) as observed for osmium, and at the same potentials as for nonsandwich films of osmium or ruthenium polymer alone, since $E^{\circ\prime}$ for the M(II/I) and M(I/0) reactions are approximately the same for both polymers. The redox conduction due to the M(III/II) reaction occurs with similar i_L (23 μA) to that with just one polymer, and it is centered on $E^{\circ\prime} = 1.22$ V vs. SSCE for the ruthenium polymer. Redox conduction is not observed at E_{Pt} near the osmium polymer $E^{\circ\prime}$. The latter is the expected result[6] since the bilayer cannot conduct electrons until both polymer films are mixed valent, which requires that E_{Pt} be close to $E^{\circ\prime}$ for the ruthenium polymer. A quantitative treatment of i_L for the bilayer is given elsewhere.[25]

The corollary result is obtained if E_{Pt} is kept constant at 0 V vs. SSCE and E_{Au} is varied. As shown in Figure 8B, a nonsteady-state wave for oxidation and reduction of the osmium part of the film is observed at the Au electrode, centered at $E^{\circ\prime}$ for the osmium polymer. No significant current is seen at the Pt electrode, which has a potential sufficient to re-reduce the Os(III) generated by the Au electrode. This is, of course, because the inner ruthenium polymer film remains as Ru(II) and is an insulator in this non-mixed-valent state.

Acknowledgment. This research was supported in part by the Office of Naval Research and by grants from the National Science Foundation and from the Chevron Research Company.

Registry No. Poly[Ru(bpy)$_2$(vpy)$_2$]$^{2+}$, 88670-65-9; poly[Ru(vbpy)$_3$]$^{2+}$, 81206-05-5; poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$, 88728-97-6.

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[25] Pickup, P. G.; Leidner, C. R.; Denisevich, P.; Murray, R. W., *J. Electroanal. Chem.*, in press.

Water-Soluble α,ω-Bis(paraquat) Amphiphiles Form Monolayer Membrane Vesicles, Micelles, and Crystals by Stepwise Anion Exchange or Photochemical Reduction

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Contribution from the Institut für Organische Chemie der Freien Universität Berlin, 1000 Berlin 33, West Germany, and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Elektronenmikroskopie, 1000 Berlin 33, West Germany. *Received July 13, 1983*

Abstract: 1,1″-[(1,8-Dioxo-1,8-octanediyl)bis(oxy-11,1-undecanediyl)]bis[1′-methyl-4,4′-bipyridinium] tetrachloride (**3a**), 1,1″-[(1,12-dioxo-1,12-dodecanediyl)bis(oxy-11,1-undecanediyl)]bis[1′-methyl-4,4′-bipyridinium] tetrachloride (**3b**), the corresponding dibromide diiodide (**3f**), 1,1″-[(1,18-dioxo-1,18-octadecanediyl)bis(oxy-11,1-undecanediyl)]bis[1′-methyl-4,4′-bipyridinium] tetrachloride (**3c**), the corresponding tetraperchlorate (**3d**), and trichloride monoperchlorate (**3e**) have been prepared. The solubility and the aggregation behavior of these compounds largely depend on the nature of the inorganic anions. The tetrachlorides **3a–c** are readily soluble in water. Titration of **3c** with 1 equiv of sodium perchlorate or irradiation of **3c** with visible light in the presence of ferrocyanide lead to vesiculation. Vesicles were also obtained by dissolving the dibromide diiodide **3f** in water. A turbid emulsion of the tetraperchlorate **3d** clears on heating to 70 °C. After cooling to room temperature vesicles were formed; after 24 h at room temperature crystals of a thickness ≤100 Å were observed in electron micrographs. This corresponds to a crystalline monolayer. The electron micrographs also show micelles of diameters ~100 Å.

Our general investigation of monolayer vesicle membranes has shown that α,ω-bifunctional amphiphiles produce unsymmetric vesicles if the size of both head groups is different.[1] Curvature is produced by orientation of the large head groups to the outside and the small head groups to the inside. An early report by our group that symmetric α,ω-bis(bipyridinium) amphiphile **1** gives vesicles[2] was partly in error. Vesicle formation rather depended

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[1] Fuhrhop, J.-H.; Mathieu, J. *J. Chem. Soc., Chem. Commun.* **1983**, 144. See also: Okahata, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1979**, *101*, 5231.

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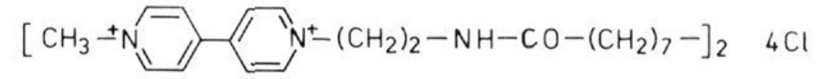

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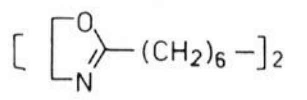

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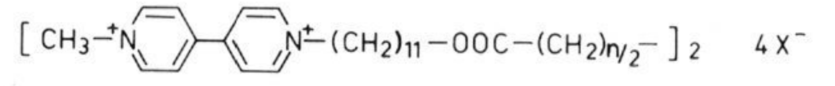
on the presence of small amounts of water-insoluble impurities such as **2**, which were byproducts in the synthesis of **1** and which have not been recognized.[3] The pure tetrachloride **1** is water soluble and does not form vesicles. We now report a new method of monolayer vesicle formation, where vesicle formation is caused by different counterions. With water-insoluble symmetric salts were produced monolayered crystals and micelles which are, to our knowledge, reported for the first time. These aggregates can reversibly be converted to monolayer vesicles.

Results

Synthesis. Since the diamide **1** is difficult to purify, we adopted a method by Fendler,[4] to synthesize paraquat diester amphiphiles **3a–f**. In our procedure 11-bromo-1-undecanol is esterified with



3	a	b	c	d	e	f
n	6	10	16	16	16	10
X/4	4 Cl	4 Cl	4 Cl	4ClO4	ClO4 3 Cl	2 Br 2 J

dicarboxylic acid dichlorides. Two moles of bipyridine then substitute the terminal bromides. Methylation with dimethyl sulfate or methyl iodide and ion exchange are the final steps. Overall yields are up to 35% and several grams can be produced in one batch.

Vesicle Formation. **3a–c** are readily soluble in water. Solutions of 10^{-1} M **3c** do not show enhanced light scattering or vesicles in electron micrographs. Water-soluble porphyrins are not entrapped.[5] Addition of 1 mol of sodium perchlorate, a "chaotropic reagent",[6] to **3c** leads to a slightly turbid solution of **3e**. Electron micrographs now show vesicles with diameters from 300 to 500 Å (Figure 1a). Entrapment of a water-soluble porphyrin, Sephadex G50 chromatography, and enhanced light scattering also indicate the presence of vesicles. On addition of potassium ferricyanide 50% of the ^{1}H NMR signals for the bipyridyl head groups (δ 9.56 and 9.02) are shifted to higher fields (δ 9.37 and 8.84) and are also broadened. These shifts are similar to the values reported by R. Hague et al. for aqueous solutions of paraquat[7] and ferricyanide. The fact that 50% of the original signal's intensity is retained indicates a monolayer vesicle with equal numbers of bipyridyl head groups in- and outside (Figure 2).

Similar vesicles are obtained by dissolving the dibromide diiodide **3f** in water (Figure 1b). The critical concentration of vesicle formation as determined by surface tension and conductivity measurements[8] is $2 \pm 2 \times 10^{-3}$ mol L^{-1}. Iodide is also known as a chaotropic anion,[6] which in our case simply means an anion which closely binds to the bipyridyl head groups. Curvature and vesiculation are presumably caused by the one-sided formation of insoluble sites (Figure 1c). The α,ω-bifunctional amphiphile

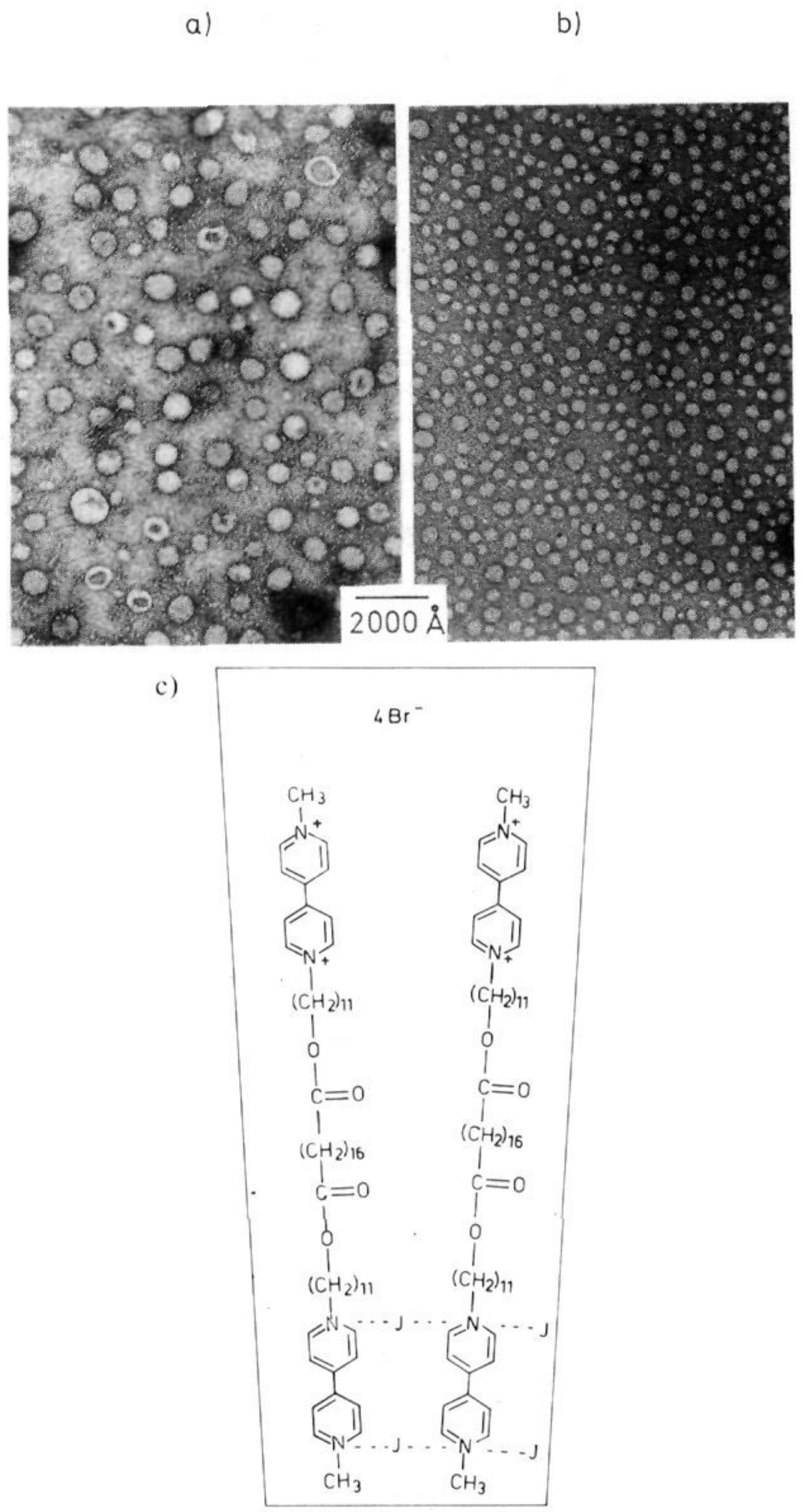


Figure 1. Electron micrographs of negatively stained (1% uranyl acetate) vesicles made from (a) the paraquat monoperchlorate **3d** and (b) the paraquat dibromide diiodide **3f** (see text). (c) Hypothetical arrangement of two neighboring amphiphile molecules in the vesicle's membrane.

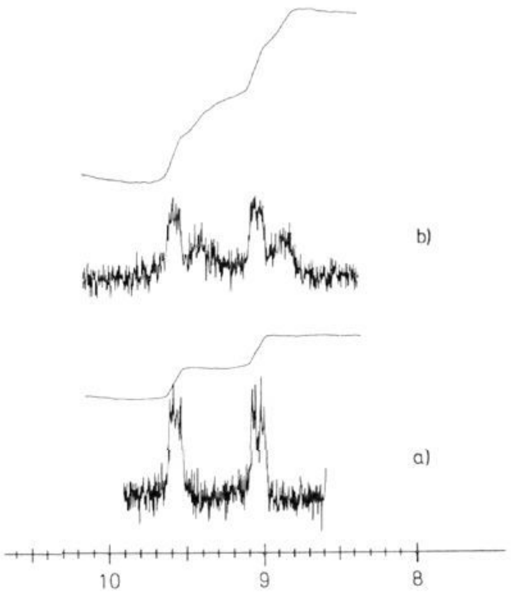


Figure 2. (a) ^{1}H NMR signals of the bipyridyl protons of compound **3e** in vesicular, aqueous solution. Internal standard: water = 5.00 ppm. (b) After addition of 0.2 equiv $K_3Fe(CN)_6$.

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(2) Baumgartner, E.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 550.

(3) Link, T. Diplomarbeit FU Berlin, 1982. **2** was not detected in the ^{1}H NMR spectrum of **1** in methanol. Its elemental analysis is close to the analysis of **1** (**1**, 10.2% N; **2**, 9.0% N).

(4) Tundo, P.; Kippenberger, D. J.; Politi, M. J.; Klahn, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 5352.

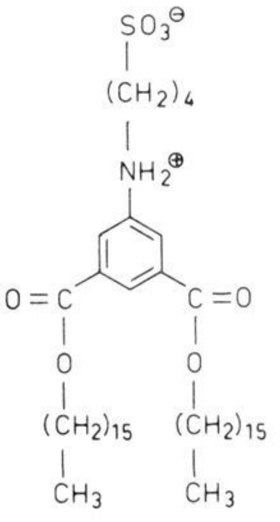
(5) The water-soluble porphyrin was the (tetraethylenediamine) protoporphyrin adduct described by Plane. (a) White, W. I.; Plane, R. A. *Bioinorg. Chem.* **1974**, *4*, 21. (b) Fuhrhop, J.-H; Krüger, W.; David, H. H. *Liebigs Ann. Chem.* **1983**, 204.

(6) Pigor, T.; Lawaczek, R. *Z. Naturforsch., C: Biosci.* **1983**, *83c*, 307.

(7) Hague, R.; Coshow, W. R.; Johnson, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3822.

(8) Shimomura, M.; Hashimoto, H.; Kunitake, T. *Chem. Lett.* **1982**, 1285.

3c is also useful as an indicator for vesicle formation. The zwitterionic amphiphile **4**, for example, gives bilayer membrane vesicles. If 1% of **3c** is added during the sonication, **3c** is quantitatively dissolved in the vesicle membrane. Reduction of **3c** in this vesicular solution gives 50 ± 5% reduction to the viologen radical. After addition of Triton X 100 the vesicle is destroyed and 100% reduction is observed. Dithionite reduction of vesicles made from pure **3f** leads to precipitation.



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Both the ^{1}H NMR shift experiments with vesicles made from **3e** and the reduction experiments in a mixture of **3c** and **4** indicate that 50 ± 5% of the bipyridyl head groups are on the outer surface. The inner surface must then be formed by the other half of the bipyridyl head groups. The observed 1:1 ratio of in- and outside head groups can only be rationalized with the stretched conformation of the α,ω-bisamphiphiles given in Figure 1c.

Vesicles can also be obtained by partial photoreduction of **3c**. A 2.8×10^{-3} M aqueous solution of **3c** containing 0.7×10^{-3} mol L^{-1} potassium ferrocyanide shows a charge-transfer band at 585 nm,[9] which shifts in daylight to 650 nm. In an ESR experiment the same 585-nm complex gives no signal, but on irradiation a radical spectrum[10] appears. Before irradiation the solution does not contain vesicles; after irradiation vesicles are observed in electron micrographs. The vesicle solution retains its blue color for several days in a closed cuvette. Solutions of nonvesicular paraquat radicals are much less stable.

Monolayer Crystals and Stable Micelles. The tetraperchlorate **3d** can be obtained as a crystalline precipitate from the tetrachloride **3c** in methanol. In water **3d** is insoluble, but a 10^{-3} M emulsion becomes clear on heating to 70 °C. The solution becomes turbid within hours at room temperature and contains vesicles of uniform size. Its electron micrographs are very similar to Figure 1a. After 24 h, however, the electron micrographs of this emulsion show platelets of a thickness <100 Å. Since **3d** is approximately 75-Å long in a stretched conformation,[11] this means that the crystal has the thickness of one molecular layer only (Figure 3a–c). To our knowledge this is the first preparation of a monolayer organic crystal. Electron micrographs of these crystals also show small particles with diameters close to 100 Å (Figure 3a,b). Their appearance is very similar to micelles which have been obtained by special rapid-freeze (10^5 °C s^{-1}) techniques.[12] In our case the micelles appear on electron micrographs of preparations which have been produced with standard techniques. Micelles of α,ω-bifunctional amphiphiles seem to be exceptionally long lived, and we tentatively describe them with the cubic structure given in Figure 3c.[13] On heating to 70 °C the crystals are again dissolved and vesicles are formed. In thermal differential analysis the crystals produce two endothermic peaks at 62 and 67 °C.[14] The vesicle membrane does not produce peaks in the thermograph. We assume that the melting process destroys the crystals and that vesiculation is kinetically favored over recrystallization. The unique thinness is presumably caused by the polar end groups and the large counterions, which favor separations of crystal layers. Our results clearly indicate that the aggregation number and curvature of the aggregates of α,ω-bis(paraquat) amphiphiles can be altered by the nature and stochiometric ratio of counterions. A monolayer structure has been demonstrated for the vesicle membranes (^{1}H NMR; 50% reduction) and is very likely for the crystals (electron microscopy). The structure of the crystals' edges and the observed stable micelles, however, remains unknown and will be further investigated.

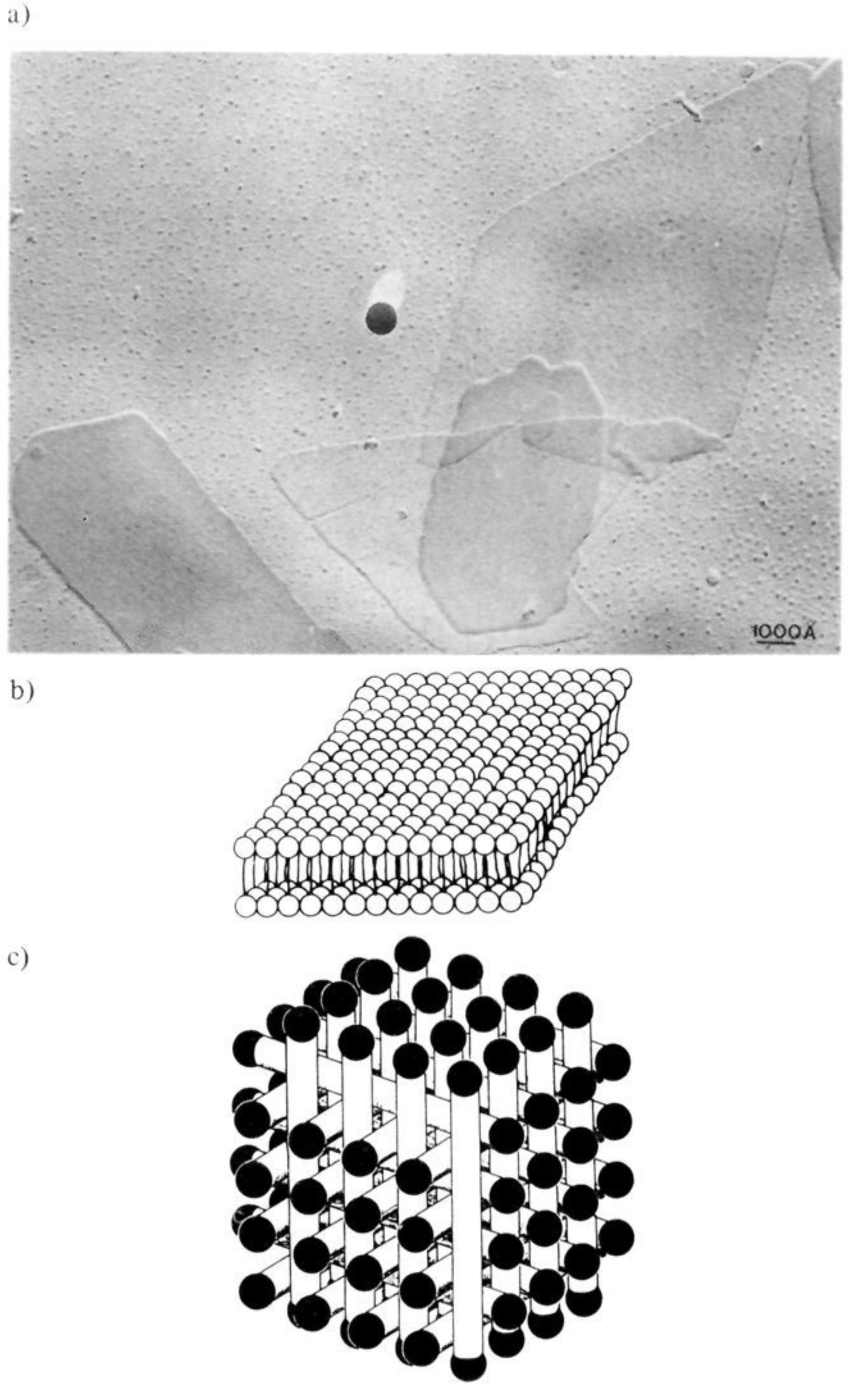

Figure 3. (a) Electron micrograph[13] of the monolayered crystals and micelles of the tetraperchlorate **3d** after freeze-drying and tungsten shadowing. The diameter of the latex particles is 900 Å. (b) Schematic structure of the crystal. (c) Schematic structure of the micelles.

Experimental Section

^{1}H NMR spectra were recorded on a 270-MHz Bruker spectrometer with chemical shifts reported on the scale relative to Me_4Si. Electronic spectra were taken with a CARY 17 D1 spectrophotometer. ESR spectra were obtained on a BRUKER B-ER 414 spectrometer and a flat, thin quartz cell. Microanalyses were performed by the Mikrolabor des

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(9) Murthy, A. S. N.; Bhardwaj, A. P. *Spectrochim. Acta, Part A* **1982**, *38A*, 207. The reported wavelength for a paraquat–ferrocyanide 2:1 complex is 550 nm.

(10) Line width 12.5 G, G = 2.00, no hyperfine splitting. Identical with ESR spectra of micellar viologen radical aggregates. See: Takuma, K.; Sakamoto, T.; Nagamura, T.; Matsuo, T. *J. Phys. Chem.* **1981**, *85*, 619.

(11) The amphiphile is 60 covalent bonds long, which were averaged to 1.25 Å each.

(12) Bachmann, L.; Dasch, W.; Kutter, P. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 883.

(13) Amphiphilic α,ω-diammonium salts have been shown to give micelles. Zana, R.; Yiv, S.; Kale, K. M. *J. Colloid Interface Sci.* **1980**, *77*, 456.

(14) Range 0.1 mcal s^{-1}. The enthalpies of transition were 98 kJ mol^{-1} at 62 °C and 65 kJ mol^{-1} at 67 °C. See: Okahata, Y.; Ando, R; Kunitake, T. *Ber. Bunsenges, Phys. Chem.* **1981**, *85*, 789.

Instituts für Organische Chemie der Freien Universität Berlin. Thermal analyses were carried out on a differential scanning calorimeter (Perkin-Elmer DSC-2C). Surface tension was measured with an interfacial tensiometer (Krüss) by the du Noüy ring detachment method. Electron micrography was performed on a Philips EM-400T electron microscope.

1,1″-[(1,18-Dioxo-1,18-octadecanediyl)bis(oxy-11,1-undecanediyl)]-bis[1′-methyl-4,4′-bipyridinium] Tetrachloride (3c). Octadecanedioic acid (4.5 g, 14.3 mmol) was dissolved in 50 mL of thionyl chloride and refluxed for 5 h. The solvent was removed, and the resulting octadecanedioyl dichloride dissolved in 50 mL of dry chloroform. This solution was added dropwise to a stirred solution of 7.19 g (28.6 mmol) 11-bromo-1-undecanol in 50 mL of dry chloroform containing 3.3 mol (28.6 mmol) of 2,6-lutidine at 0 °C. After 30 min at 0 °C the solution was stirred for 3 h at room temperature. The solvent was removed and the residue extracted 5 times with hot hexane (~1 L). The combined extracts were decolorized with alumina; and the solvent was evaporated to 500 mL. Crystallization at 0 °C yielded 7.3 g (66%) of white microcrystals of octadecanedioic acid bis(11-bromoundecyl) ester (mp 58 °C).

This α,ω-dibromo ester (6.0 g, 7.7 mmol) was refluxed for 3.5 h in nitromethane with 7.2 g (46 mmol) of 4,4′-bipyridine. After cooling to room temperature the product precipitated and was recrystallized from *n*-butanol, yielding 6.4 g (76%) of white platelets (mp 131–133 °C).

This bis(bipyridinium) salt (5.4 g, 4.9 mmol) was dissolved in 100 mL of nitromethane at 60 °C. An excess (1.4 mL, 15 mmol) of dimethyl sulfate was added and stirred for 3.5 h at 60 °C. After standing overnight at room temperature it was cooled in an ice bath. The crude product precipitated. It was redissolved in methanol and filtered over Amberlite C 64001 to give the tetrachloride **3c** after two crystallizations from methanol. Yielding 3.5 g (65%) of slightly yellow-brown microcrystals: mp >250 °C; ^{1}H NMR (CD_3OD) δ 9.30 (d, 4 H), 9.20 (d, 4 H), 8.68 (m, 8 H), 4.75 (t, 4 H), 4.53 (s, 6 H), 4.05 (t, 4 H), 2.30 (t, 4 H), 2.10 (m, 4 H), 1.61 (m, 8 H), 1.32 (m, 52 H); UV max 259 nm (ϵ 39400). Anal. Calcd for $C_{62}H_{98}Cl_4N_4O_4$: C, 67.37; H, 8.94; N, 5.07. Found: C, 66.9; H, 9.0; N, 4.7.

1,1″-[(1,18-Dioxo-1,18-octadecanediyl)bis(oxy-11,1-undecanediyl)]-bis[1′-methyl-4,4′-bipyridinium] Tetraperchlorate (3d). A concentrated methanolic solution of **3c** was mixed with an excess of lithium perchlorate in methanol. **3d** precipitated and was recrystallized from methanol/ethanol.

Anal. Calcd for $C_{62}H_{98}Cl_4N_4O_{20}$: C, 54.70; H, 7.26; N, 4.12. Found: C, 54.64; H, 7.28; N, 4.13.

Typical vesicle formation involved the dissolution of **3c** in distilled water (10^{-3} M) and titration with sodium perchlorate solution. After addition of 1 equiv of this salt the solution became slightly turbid. To separate a water-soluble porphyrin[5] from vesicles made from **3e** a G 50 Sephadex column (h = 20 cm, ϕ = 1 cm) was used. This was first saturated with the tetrachloride **3c** and washed with distilled water. The vesicles containing the porphyrin in the inner water volume separated in a sharp band from the free porphyrin on such presaturated columns. Without presaturation[15] the vesicle fraction smeared over the whole column.

Electron micrographs were taken after adsorbing the amphiphilic aggregates on a carbon film (thickness 40 Å), applying a gentle procedure of freeze-drying and tungsten shadowing.[16] The length of sharply delineated shadows (e.g., Figure 3a) of latex particles was taken as a measure for the thickness of the crystals and micelles. Negative staining with uranylacetate was also performed on the same carbon films.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Förderungskommission für Forschung und wissenschaftlichen Nachwuchs der Freien Universität Berlin is gratefully acknowledged (FGS Biomembranen). We also thank Dipl.-Chem. Gustav Penzlin for a drawing.

Registry No. 3a, 88888-76-0; **3b**, 88904-46-5; **3c**, 88888-77-1; **3d**, 88888-79-3; **3e**, 88888-80-6; **3f**, 88904-47-6; bis(11-pyridinioundecyl)-octadecanedioate dibromide, 88888-81-7.

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(15) Huang, C.-H. *Biochemistry* **1969**, *8*, 344.
(16) Tesche, B. *Mikroskopie* **1978**, *34*, 29.

A One-Dimensional Polymeric Ribbon Alternative to the Aggregation of d^8 ML_4 Fragments

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853, and the Arthur Ames Noyes Laboratory, California Institute of Technology, Pasadena, California 91125. *Received July 12, 1983*

Abstract: d^8 ML_4 fragments normally trimerize, as in $Os_3(CO)_{12}$, or stack, as in $Pt(CN)_4^{2-}$. There is an alternative to these aggregation modes. Still unobserved, but not unreasonable, is the formation of a one-dimensional infinite ribbon, stoichiometry ML_2X, with X bridging and a zigzag single-bonded metal chain, **6**. The detailed analysis of the band structure of this material is the subject of this work.

Think about the d^8 ML_4 fragment. Two geometries are likely for it, the angular **1**, an octahedron minus two cis ligands, and the flat **2**, an octahedron minus two trans ligands. If one examines the possible realizations of this fragment, from Fe, Ru, Os(0) through Co, Rh, Ir(I) to Ni, Pd, Pt(II), and Cu, Ag, Au(III), one realizes that the angular **1** is favored for low oxidation states and the flat **2** for the more electronegative high oxidation states of the late transition metals. The reasons for this preference are reasonably well understood (see Appendix).

A further difference emerges between the angular and flat fragments if we think about their kinetic and/or thermodynamic stability. **1** is not stable, but typically trimerizes to **3**, as for $Os_3(CO)_{12}$.[1] **2** is usually kinetically and thermodynamically stable as the monomer, e.g., $Pt(CN)_4^{2-}$. But for certain square-planar d^8 complexes there is a definite tendency to one-dimensional

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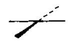

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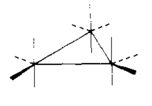

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[†] Cornell University.
[‡] California Institute of Technology.

(1) Corey, E. R.; Dahl, L. F. *Inorg. Chem.* **1962**, *1*, 521–526. For $Ru_3(CO)_{12}$ see: Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1978**, 778–779.

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