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DIMERIZATION OF METALLATED PIGMENTS AS PRIMARY STEP IN THE CONSTRUCTION OF MEMBRANE GAPS ON GOLD, POLYMERIC WIRES AND ISOLABLE MICELLES

Jürgen-Hinrich Fuhrhop*, Christoph Böttcher, Christian Draeger, Werner Fudickar,
Andrea Schulz, Christian Messerschmidt

Institut für Organische Chemie des Fachbereichs für Chemie, Biologie und
Pharmazie der Freien Universität Berlin
Takustraße 3, D-14195 Berlin, Germany

Jörg Zimmermann

Institut für Physik der Mathematisch-Naturwissenschaftlichen Fakultät (Physik,
Chemie, Pharmazie und Biologie) der Humboldt Universität
Invalidenstr. 110, D-10115 Berlin, Germany

Abstract: β-Octasubstituted porphyrins form face-to-face dimers in solution, which are stabilized by π–π' interactions in case of π-radical formation. Polymerization of viologen substituted zinc porphyrins leads depending on stereochemistry to micelles or wire pairs. Anionic porphyrins were also adsorbed to gold electrodes or colloids and entrapped in membrane gaps. Heterodimerization of these porphyrins adsorbed to solid phase surfaces and entrapped within a 2 nm membrane gap was detectable by fluorescence quenching. Ruthenium complexes with two bipyridyl and one dioctadecyl dipyridyl methylene malonate ligand form head-to-head dimers in aqueous solution. The octadecyl substituents of the dimer constituents point to opposite directions and large multilayer micelles are formed upon aggregatetion in water. They survive drying. Dimerization processes are discussed as common basis for the formation of four uncommon supramolecular assemblies

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INTRODUCTION

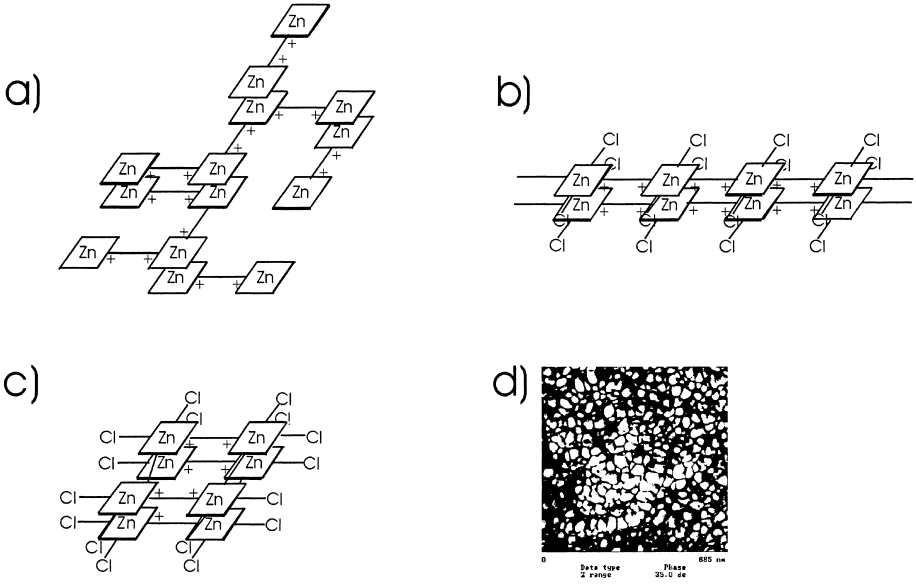
Metal complexes of dye ligands often provide exceptionally large surface areas, which favor the formation of dimers and/or polymers by strong van der Waals interactions Typical examples are metalloporphyrins, with just one large planar ligand molecule and octahedral ruthenium dipyridyls with three ligand molecules forming approximately a cube.

The formation of metalloporphyrin fibers by stacking and lateral binding of polar substituents has been discussed in two earlier papers in this series[1]. Here we evaluate the formation of molecular wires from zinc octaetylporphyrin radicals or dications[2,3] bearing viologen-type substituents in one *meso*-position[2,3] and the role of heterodimers in surface reactions[4,5]. It will be shown, that defined porphyrin dimers are useful to as units for the formation of uniform supramolecular assemblies and provide size-selective fluorescence quenchers in work on rigid membrane gaps mimicking reactive surface clefts in enzymes.

Amphiphilic ruthenium dipyridyl complexes are, under appropriate conditions, fluorescent and provide redox active systems upon irradiation with visible light. Polymeric assemblies of corresponding amphiphiles have been studied so far in form of planar molecular monolayers on water[6,7] and entrapped in zeolites[8]. We discuss here the peculiar formation of back-to-back dimers of unsymmetric ruthenium dipyridinyl complexes containing one unit with a methylene bridge bearing a dioctadecylmalonate substituent. A double-comb structure is the result of this reaction and its self-organization leads to stable, multilayered micelles[9].

RESULTS

A saturated acetonitrile/1,2-dichloroethane solution of meso dipyridyl zinc octaethyl porphyrin (~ 10^{-3} m) was oxidized with an ITO-electrode to the dication. The terminal pyridine unit added another porphyrin and zig-zag polymers were formed, because the substitution could occur either on the methine bridges adjacent or opposite to the first dipyridyl substituent. Since zinc octaethyl porphyrin always appears as a cofacial dimer in solution, the polymer is also an irregular net of polymer chains in two planes (Figure 1a)[10]. AFM shows water-swollen bilayers with the appearance of vesicle assemblies (Figure 1d). If the zig-zag growth is blocked by substituting opposite methine bridges of the porphyrin with chlorine, then linear growth of the polymer is enforced (Figure 1b). The resulting polymer appears as a pair of parallel running wires under the electron microscope. These wires are several micrometers long, which means that each of them has polymerization grades in the order of 10^4. This is an extraordinary high molecular weight and ordering for polymers made of dye molecules. We assume that interrupted growth, which occurs on one polymer strain is repaired by using the parallel running strain as a matrix. Porphyrin **1** dimer thus polymerizes with statistical order in two planes, whereas the same dimer of the dichloro compound **2** undergoes only linear and parallel growth yielding two perfect wires. The third possible case, namely exclusive orthogonal growth would lead to a doublet of cyclic tetramers. Single helices or a double helix of parallel running strands should be formed. But this has not been verified yet (Figure 1c).



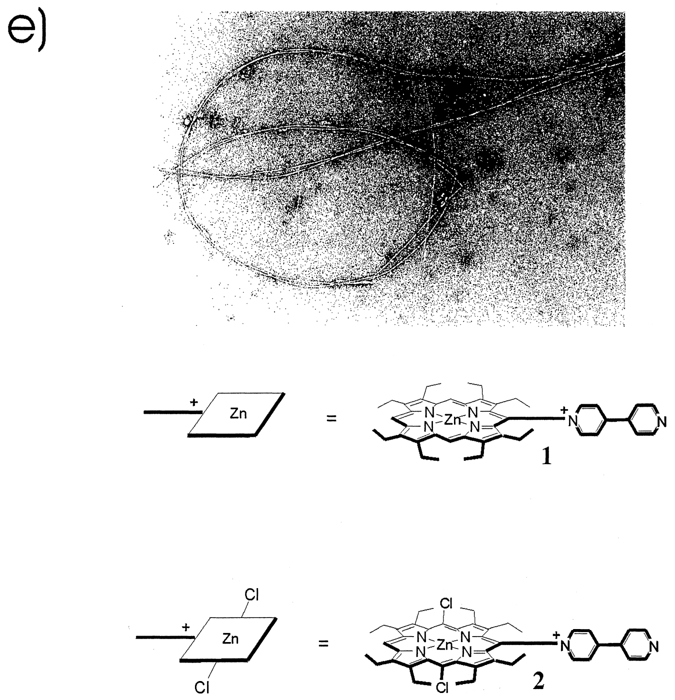


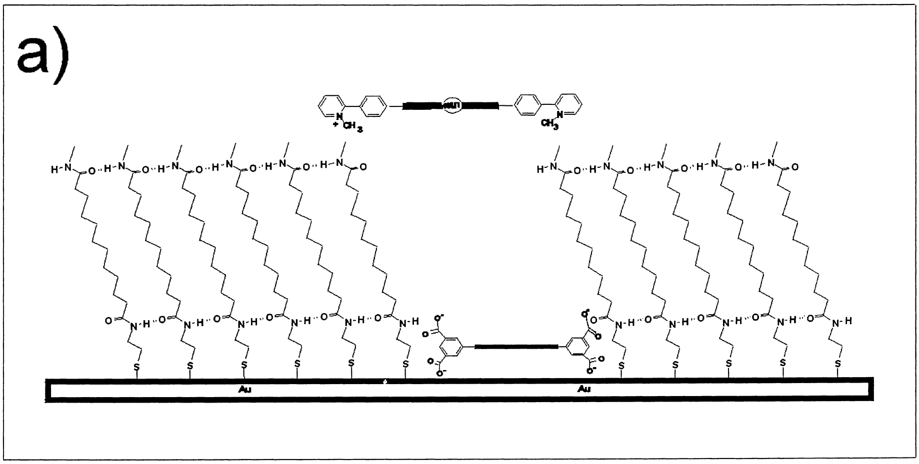
Fig. 1 Polymerization pattern and atomic force micrographs of *meso*-bipyridinium zinc octaethylporphyrinates on the surface of an ITO (=indium tin oxide) electrode.

a) Irregular zig-zag pattern upon orthogonal (5,15) and linear (20) substitution of **1**.
b) Formation of dimeric wires upon 20-substitution of **2.**
c) Hypohelical double helix formation upon substitution of C-15 in a 5,20-dichlorinated zinc complex (not shown).
d) Vesicular polymers made from **1** (AFM = atomic force microscopy).
e) Linear polymers obtained from **2** (TEM = transmission electron microscopy)).

Dimerization of porphyrins has also been used in the construction of functionalized membrane gaps. β-Tetrapyridiniumporphyrins form dimers with *meso*-tetraphenylsulfonatoporphyrins in water if further aggregation to polymeric stacks is impeded by extra β-ethyl groups. The binding constant of the dimer in water is between 10^6 and 10^8 M. If one of the constituents is a Mn(III) or Cu(II) complex, total fluorescence quenching occurs upon dimerization[10,11].

An octaanionic porphyrin was self-assembled on gold electrodes or spherical gold colloids and still showed strong fluorescence. Addition of tetracationic manganese porphyrin counterions in water quenched this fluorescence quantitatively, independent of the size of the porphyprin. Only the position of the interacting charges had to be adjusted in the right way. The same quenching occurred if the porphyrins on gold were embedded in a soft matrix of octadecylthiol.

Then the porphyrin-based gap was "rigidified" by the introduction of amide hydrogen bond chains in the membrane. As a result, only the fitting anionic manganese porphyrin found its way through the membrane gap quenching was observed. Larger porphyrin anions could not enter, and fluorescence remained stable upon addition of the corresponding manganese complex (Figure 2). Such a size-dependent recognition process in membrane gaps can easily be verified with large metal complexes and is next to impossible with linear dye molecules[12].



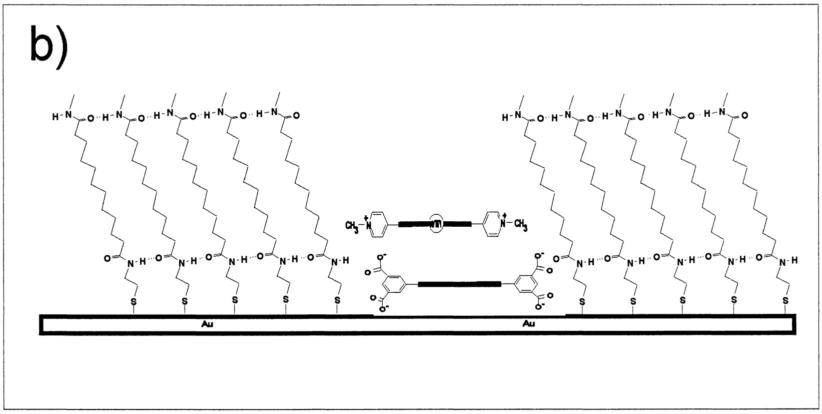


Fig. 2: Application of porphyrin heterodimer formation in the characterization of rigid membrane gaps which differentiate the size of porphyrins.

(a) The large manganese(III) porphyrinate with three extra phenyl spacers is rejected, whereas.

(b) the fitting manganese(III) porphyrinate finds its way to the porphyrin on the bottom of the membrane gap and quenches its fluorescence.

In basic aqueous solution (pH 12) manganese porphyrin dimers are also useful to produce molecular oxygen[11,13]. Four-electron reduction occurs quite efficiently.

As a final example for the importance of the structure of the primary dimer in defined aggregation processes, we shall discuss the mesoscopic micellar structure obtained from the ruthenium complex **3**. It is soluble in the form of small micelles in water as long as the counterions for the ruthenium dication are bromide anions. Titration with perchlorate or hexafluorophosphate gives mesoscopic, multilayered micelles, which have been characterized by low-dose electron microscopy (Figure 3a)[9]. If one considers the ruthenium head group of **3** as a cube with a side length of 1 nm then the two alkyl chains and two connecting PF_6-counterions occupy five planes of the cube. The sixth plane is free for head-to-head dimer formation. As a result, one obtains a head group region , which contains two back-to-back oriented head group and alkyl chains on both sides (Figure 3b). The large difference between the head group and alkyl chain cross section areas enforce interdigitation of the latter. One obtains 23 Å thick interdigitated alkyl bilayers and 23 Å thick head group layers. This is exactly what is observed in the electron micrograph. Both structural elements lead to an extreme stabilization of the mesoscopic micelle which is obtained. It survives drying as well as deposition on a solid surface, as shown by AFM of the micelles on mica (Figure 3c).

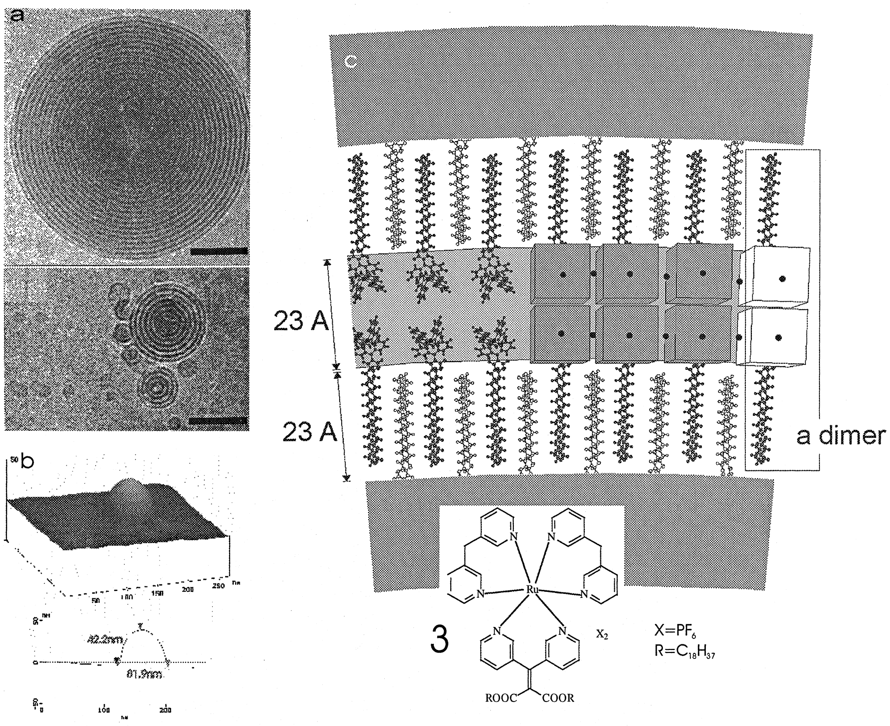


Fig. 3: (a) TEM of the multilayered micelle made of **3.**
(b) AFM of the same micelles on mica in the dry state.
(c) Molecular model of an interdigitated bilayer made of head-to-head dimers of **3**.

CONCLUSION

Dimerization and heterodimerization of amphiphilic metal complexes in water is by no means only dictated by connecting axial ligands. The whole architecture of their molecular assemblies can also be dominated by the primary event of the ligand dimerization in solution. The self-organization of such dimers to polymeric assemblies then leads to five out of five possible membrane structures[14] in the order of growing curvature:

(i) planar monolayers on fluid or solid surfaces
(ii) vesicular fibers
(iii) spherical vesicles
(iv) micellar fibers and

(v) spherical micelles.

Each of these assemblies may constitute a solid, isolable material, if the monomers are connected by directed, non-covalent bonds, e.g. hydrogen bond chains or localized ionic bonds. Only toroids have, so far, not been obtained from metal complexes..

The kind of polymeric assembly, which is formed by a given metal complex dimer is difficult to predict. It depends very much on the relative arrangement of the water-soluble head groups and water-insoluble skeleton.

In case of quasi cubic ruthenium complexes with tightly bound PF_6^- counterions, the head groups stick together at the side bearing the alkyl chains and the bis-dipyridyl side. A double-comb is formed and the interdigitation of the octadecyl chains leads to multilayered micelles which can be isolated in the dry state. The ultimate curvature of the central micelle removes the interdigitation and enforces a high water content. Long-term stabilization, however, is again achieved by dimerization of the head groups and coverage with a less curved interdigitated bilayer (Figure 3).

Dimers of planar metalloporphyrin amphiphiles, on te other hand, cannot turn one polar head group up, the other down. Both will essentially remain in one plane and formation of a stable spherical micelle is not possible. Stacking of the hydrophobic porphyrin ligands and rotation of the polar head groups favors allows, however, formation of LB-monolayers as well as of vesicles and fibers. The fibers can again be isolated and stored in dry form, if they are stabilized by amide hydrogen bond chains[1,15-17]. A spherical vesicle in general collapses upon drying, but it can be isolated if the hydrophobic porphyrin core is combined with rigid carotenoid sticks. An ion-permeable, stiff vesicle membrane is then formed, which is osmotically inactive and can be isolated in dry form[18]. This particular assembly is, however, not based on dimers, since highly substituted *meso*-tetraphenylporphyrin planes cannot approach each other.

The character of linear fibers, on the other hand, is dominated by more or less repulsive interactions between polar substituents, e.g., $-NH_3^+$, lead to micellar fibers, whereas neutral substituents, e.g. $-NH_2$, favor vesicular fibers[16]. In the ammonium case rotation of the porphyrin planes by 60-90° should occur in order to allow the formation of individual hydration spheres for each ion pair. Micellar fibers with high curvature are observed. Neutral amino groups may stay much closer together, rotational displacement and curvature are less pronounced. Vesicular fibers with a water-filled inner volume of about 30 nm are then seen in TEM.

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