

Recent advances in organometallic amphiphiles

Wang Chuanzhong, [Huang Jianbin](#), Tang Shihua
(Institute of Physical Chemistry, Peking University, Beijing 100871, China)

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Abstract Organometallic amphiphiles are new class of surfactants. Various novel chemical and physical properties of their aggregates, such as selective binding to metal ions, active control of interfacial tension, catalytic behavior and charge transfer, have been widely investigated in recent years. These interesting properties are reviewed in this paper.

Keywords Organometallic amphiphile, Surfactant, Aggregation

1. INTRODUCTION

The research of organometallic amphiphiles is interesting and important, since it combines several areas of modern science such as organometallic chemistry, coordination chemistry and surface science. Organized molecular assemblies such as micelles, vesicles and monolayers formed from organometallic amphiphiles, have attracted many chemists' attention for constructing supramolecular catalytic system, growing size-quantized semi-conductors and other functions. It was thought that the research around organized assemblies from organometallic amphiphiles is a promising work due to their unique properties, including selective binding to metal ions, active control of interfacial tension, catalytic behavior, charge transfer, etc. In this article an overview of them is presented to broaden the knowledge of us.

2. SELECTIVE BINDING TO METAL IONS

Recently, organized assemblies containing metal ions have attracted much attention for selective binding to metal ions and developing ion sensors from both fundamental and practical viewpoints. Most of interests are devoted to interaction between monolayers and metal ions in the subphase. Apart from the widely used fatty acids^[1], some amphiphiles functionalized by crown ether^[2], imidazole^[3] and iminodiacetate^[4] have been designed as monolayer-forming reagents and their interactions with metal ions in the subphases have been studied.

A long-chain thioazolylazo dye 5-octoadecyloxy-2-(2-thiazolylazo)phenol (abbreviated as TARC18) as an amphiphile to form monolayer^[5] were designed by H. Nakahara et al (Figure 1), and the relationship between surface pressure-area

isotherms of the monolayer on aqueous subphase containing Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions was studied. The monolayer forms a 1:1 complex with all the above divalent transition metal ions, and Cu(II) ion shows the strongest binding ability to the monolayer. Copper(II) ion predominately binds to the monolayer when all the above metal ion coexist in the aqueous subphase. The monolayer on the mixed ion subphase was scraped onto clean quartz plates and their components were analyzed by an inductively coupled plasma (ICP) method. The metal contents in such scraped films are listed in Table 1. The quantity of the copper (II) ion is far more than the others, so the TARC18 monolayer shows a high selectivity to Cu(II) ion.

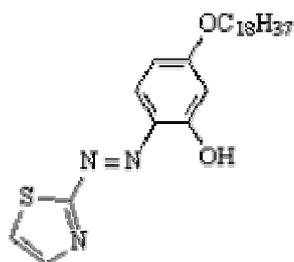


Figure 1. The Structure of TARC₁₈

Table 1. Metal Contents in the Scraped Films from the Monolayers on Aqueous of Metal Ions (ppm)^{a)}

	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
subphase I	0.36	0.80	0.66	5.82	0.85	0.63
subphase II	0.24	0.14	0.25	4.85	0.28	0.28

^{a)} Subphase I: mixture of each 0.5 mM Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II).

Subphase II: mixture of each 0.1mM Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II).

Another surface-active molecule, Kemp's triacid, has been identified as a complexing agent for heavy metal ion, such as lead and copper^[6] (Figure 2). This unique molecule may be utilized for removal of toxic metal and metal-complexation properties.

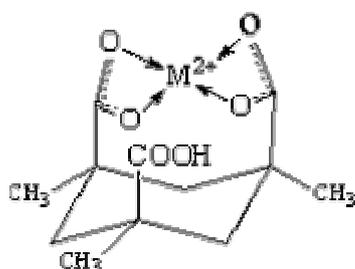


Figure 2. The complex of metal ion and Kamp' triacid

3. ACTIVE CONTROL OF INTERFACIAL PROPERTIES

Switchable control of bulky solution properties of surfactants by physical or chemical

method (such as chemical redox, electrochemical redox, light, etc) has attracted considerable interest from various viewpoints. The experimental experience in the study of redox-reversible system leads chemists to suspect that similar principles could be applied to aggregation behavior. In particular, a compound with two non-polar ends may be converted into an amphiphile by reaction of one end, if chemically switchable, with either an oxidizing or reducing agent. The resulting altered structure, if amphiphilic, might then aggregate under appropriate conditions. Such a possibility was explored by Graetzel and his co-workers who prepared an amphiphilic cyclam derivative rendered "switchable" by incorporation of a copper ion^[7]. These novel organometallic amphiphiles formed micellar aggregates.

S. Munoz and G. W. Gokel synthesized a nickel(II) phenanthroline complex 1 (Figure 3)^[8] to form vesicles in aqueous solution. The vesicles were characterized by dynamic light-scattering technique. When aqueous solution of Ni complex in Tris ·HCl buffer was treated with an aqueous solution of Na₂S₂O₄, the vesicles collapsed completely. It is because that the reduction of transition metal complexes of phenanthroline occurs at the ligand rather than at the metal center. Two electrons reduction gives an intramolecular ion pair of inherently low charge density. Reduction of the hydrophilic headgroups diminishes or eliminates monomer amphiphilicity and ultimately leads to deaggregation of the assemblies.

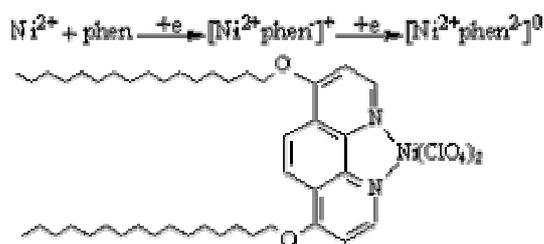


Figure 3. The complex of Ni²⁺ and twin-tailed phenanthroline derivative

Similarly the vesicles formation from 2 and 3 (Figure 4) and their redox disassembly were investigated. The results show that oxidized amphiphiles readily form vesicles. After addition of a reducing agent, the monomer loses its amphiphilic character, and causes the aggregates to collapse.

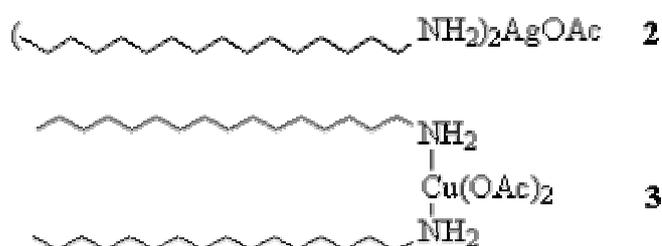
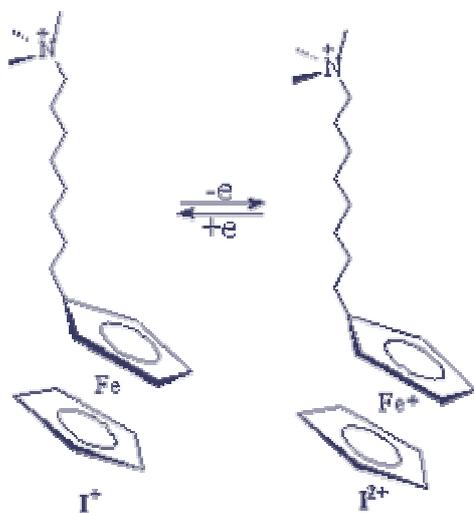


Figure 4. The metal-hexadecylamine complexes

In the meantime, the principles for *in situ* and reversible control of the interfacial properties of surfactant-based systems were established in order to make possible active control of phenomena such as the stability of thin films of liquid, the spreading or wetting of fluids on solid surfaces, and the transport of solutes across interfaces.

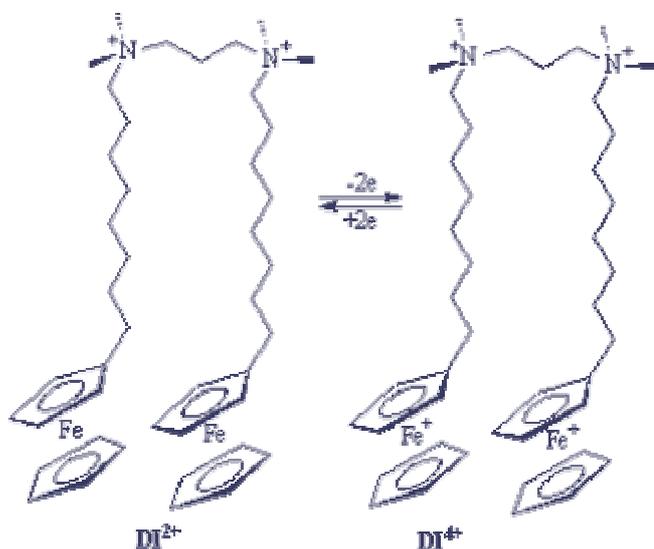
N. L. Abbott et al reported a method for active control of the surface properties of aqueous solutions by using electrochemical techniques in combination with redox active ferrocenyl surfactants $\text{Fc}(\text{CH}_2)_n\text{N}^+(\text{CH}_3)_3\text{Br}^-$ ($n=8$ [I^+], 11, 15)^[9] (Scheme I).



Scheme I

Electrochemical oxidation of ferrocene to ferrocenium (or reduction of ferrocenium to ferrocene) caused reversible changes in surface tension as large as 23mN/m.

A dimer, ferrocenyl surfactant (DI^{2+}) (Scheme II) with more unique properties have also been synthesized.



Scheme II

The surface activity and micellization of DI^{2+} were compared and constructed to those of the monomer I^+ in aqueous solution. The experimental results showed that oxidation of DI^{2+} to DI^{4+} made possible changes in surface tension of 21mN/m over a range of concentrations that exceeded an order of magnitude (0.02-0.4mM). Control of the oxidation state of I^+ , in contrast, permits changes in surface tension of about 20mN/m at one concentration (2.0mM) only (Figure 5).

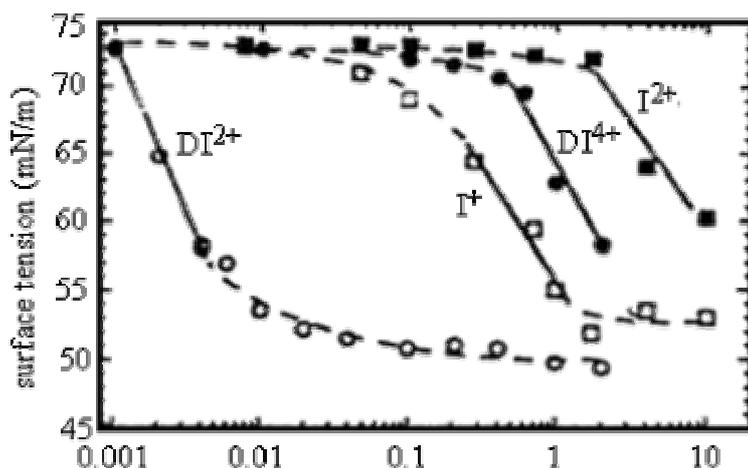


Figure 5. Equilibrium surface tensions of aqueous solutions of dimeric and monomeric ferrocenyl surfactants in oxidized and reduced states: DI^{2+} ; DI^{4+} ; I^+ ; I^{2+} . All measurements were performed in aqueous solutions of 0.1M Li_2SO_4 at 25°C and pH 2.0

Dimeric redox-active surfactants in combination with electrochemical method do, therefore, permit active control of interfacial properties of aqueous solution over a wider range of surfactant concentrations than is possible with the corresponding monomeric redox-active surfactant.

Gradients in surface tension, established by electrochemical formation of surface active species in spatially localized (smaller than millimeter) regions, have been used to direct the motion of fluid across the surfaces of solution.

4. CATALYTIC BEHAVIOR

Micelles of amphiphiles often catalyze chemical reactions, which have been attracting chemists' attentions.^[10] Recently there is continuous interest in the hydrolysis of phosphate ester, because that 1) highly toxic derivatives belong to this class of compounds, and 2) nucleic acid bases are hold together by phosphate bonds. Powerful catalysts of the cleavage of these esters may be exploited as useful detoxification reagents or as antibiotics as well.

Organometallic amphiphiles proved particularly effective in the cleavage of lipophilic triester in aqueous solutions where they form micellar aggregates (metallomicelles). One of the most effective metallomicellar systems, introduced by Menger in 1987^[11], is based on the $Cu(II)$ complex of N-n tetradecyl-N,N'-N'-Trimethylethylenediamine(TMEDC₁₄) 4 (Figure 6).

It is reported that TMEDC₁₄ possesses a remarkable catalytic activity in hydrolysis of phosphotriester. The 4-promoted hydrolysis is more than 200 times faster than the hydrolysis of 5 catalyzed by an equivalent concentration of a nonmicellar homologue, Cu^{II} -tetramethylethylenediamine complex 6. They also showed that nerve gases, such as soman 7, were very efficiently detoxified with 4 at pH 7.0 (detected by the release of F⁻). The possible reasons for the rate accelerations were the enhanced electrophilicity of the micellized copper(II) ion, the acidity of Cu^{II} -bound water, or the

intramolecular type of reaction due to the micellar formation. The $\text{Cu}^{\text{II}}\text{-OH}^-$ species 4b were postulated to be an active catalytic species. On the basis of the rate-pH profile for pH 6.0-8.3, the pK_a value for the acidity of $\text{Cu}^{\text{II}}\text{-OH}_2(4a) \rightleftharpoons \text{Cu}^{\text{II}}\text{-OH}^-(4b) + \text{H}^+$ was estimated to be less than 6.

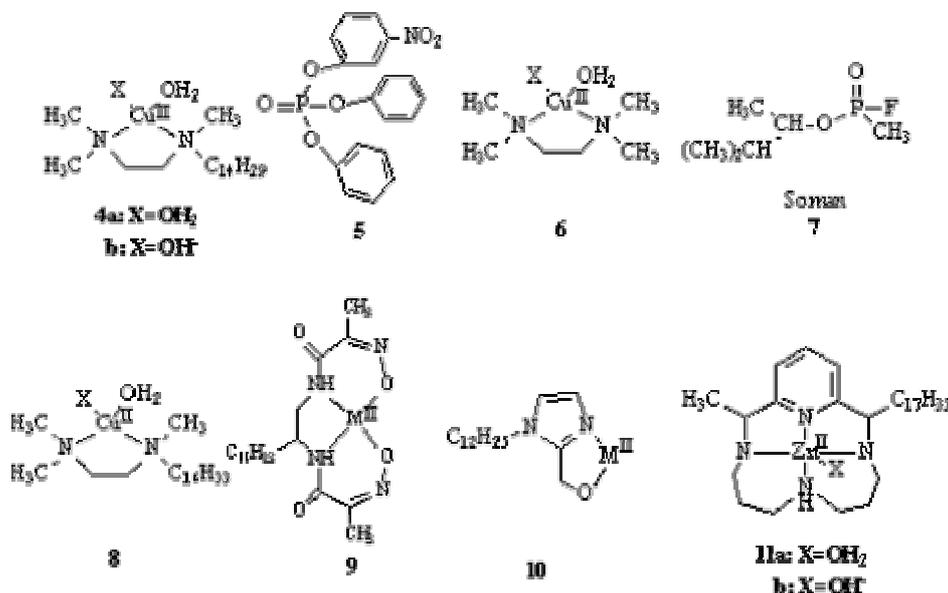


Figure 6. The structure of catalysts and substrates

R.A. Moss et al^[12] have performed a deeper research work on this area, and prepared an organometallic amphiphile TMEDC₁₆-Cu(II) 8. Compared with monomeric metalocatalysts, micellar TMEDC₁₆.Cu(II) leads to higher accelerations than 6, because that all of the substrates studied in the explored concentration favorably insert into the aggregate pseudophase where there is a high local concentration of metal complex. C.D.Gutsche et al^[13] observed that a lipophilic dioxime metal complex such as 9 (M=Cu, Ni and Zn) at pH 11.5 accelerates the hydrolysis of acetyl phosphate under comicelle-forming conditions with cetyl trimethylammonium bromide. W.Tagaki et al^[14] synthesized surfactant imidazole ligands which, in the presence of Cu^{II} and Zn^{II} (a possible structure 10), catalyzed the hydrolysis of 4-nitrophenyl picolinate in a comicellar system with hexadecyl trimethylammonium bromide. S.H.Gellman et al^[15] synthesized a lipophilic macrocyclic zinc(II) complex 11, which was an effective catalyst for the hydrolysis of phosphotriester 5 in a Brij micelle [neutral surfactant, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$]. The active species was presumed to be $\text{Zn}^{\text{II}}\text{-OH}^-$ species 11b from the sigmoidal profile of the rate-pH plot with a kinetic pK_a value of 9.1.

E. Kimura^[16] and his coworkers synthesized a cyclen derivative attached to a long alkyl chain ($\text{C}_{16}\text{H}_{33}$), as shown in Figure 7. Anticipated supramolecular assemblies between the zinc(II) complex and lipophilic substrates that coexist in micelles could make hydrolysis of lipophilic ester more effective. The experiment revealed that the active species was estimated to be $\text{ZnL}\text{-OH}^-$ rather than $\text{ZnL}\text{-OH}_2$, and the hydrolysis of TNP is 290 times more efficient than with $\text{ZnL}'\text{-OH}^-$.

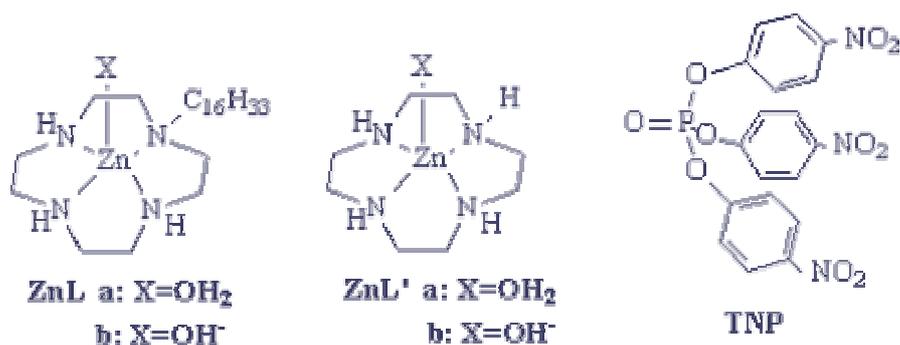


Figure 7. The structure of ZnL, ZnL' and TNP

Other catalytic systems were also investigated. For example, H.Chen et al^[17] studied olefin hydroformylation by water-soluble rhodium complexes with TPPTS (tri(*m*-sulfonphenyl)phosphine) as ligand.

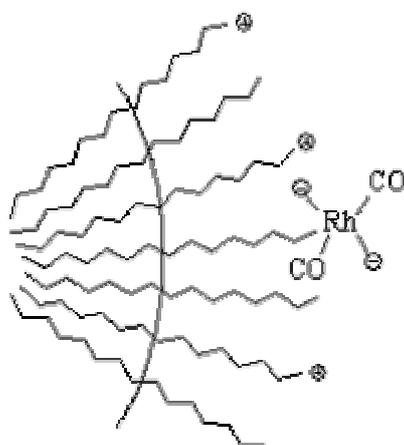


Figure 8. Rhodium complexes in micelle

Their study demonstrated that 1-dodecene hydroformation in biphasic catalytic system occurred in the interface of aqueous/organic phase. The formation of micelle was not only favorable for the reaction acceleration, but also favorable for the increase of linear aldehyde ratio in products. The key factor of the enhancement of reaction rate was the richness of rhodium electricity attraction between active rhodium anion species and cation end of surfactant.

5. ELECTRON TRANSFER REACTION

There is much current interest in the design and study of vectorial photoinduced electron systems using micelles and vesicle membranes in aqueous media. In these systems, the photoactive centers, namely synthetic porphyrin derivatives, play a crucial role,^[18] which has been widely reported.

T. Komatsu^[19] reported a bolaamphiphilic meso-tetrareesorcinolporphyrins with eight octadecyl- ω -phosphocholine side chains (octopus porphyrin, Figure 9(1)), which formed either monolayers or open fiber structure. The fibers fluoresced strongly, and laser flash photolysis lead to electron transfer from the porphyrin to hydrophobic phenyl-*p*-benzoquinone as well as to hydrophilic

1,2-naphthoquinone-4-sulfonate and dimethyl viologen acceptors.

Photoinduced electron transfer between porphyrins has also been investigated. T. Yanagimoto^[20] found significant photoinduced electron transfer reactions between lipidporphyrinato-zinc(II) (12) and iron(III) (13) complexes (Figure 9(2)) in their molecular assemblies. The self-assembled micelles of 12 and 13 showed negligible fluorescence of the photodeactive complex between the two chromophores in the ground state. On the other hand, 1,2-dimyristoyl-sn-glycero-3-phosphatidylcholine (abbreviated as DMPC) vesicles embedding the two chromophores at moderate ratios represented photoinduced electron transfer. Because of the low mobility and high dispersibility of the lipidporphyrins anchored into the gel state of DMPC membrane, the Stern-Volmer plots for the fluorescence lifetime showed a straight line up to high concentrations of the quencher; the quenching rate constant was estimated to be $1.2 \cdot 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. The electron transfer presumably occurs by a tunneling mechanism when the nearest neighboring 13 exists in the quenching sphere of 12. A Stern-Volmer analysis of the triplet quenching again exhibited a linear relationship. The estimated quenching constant was $6.2 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which was rate-limiting by the diffusion reaction in the DMPC membrane.

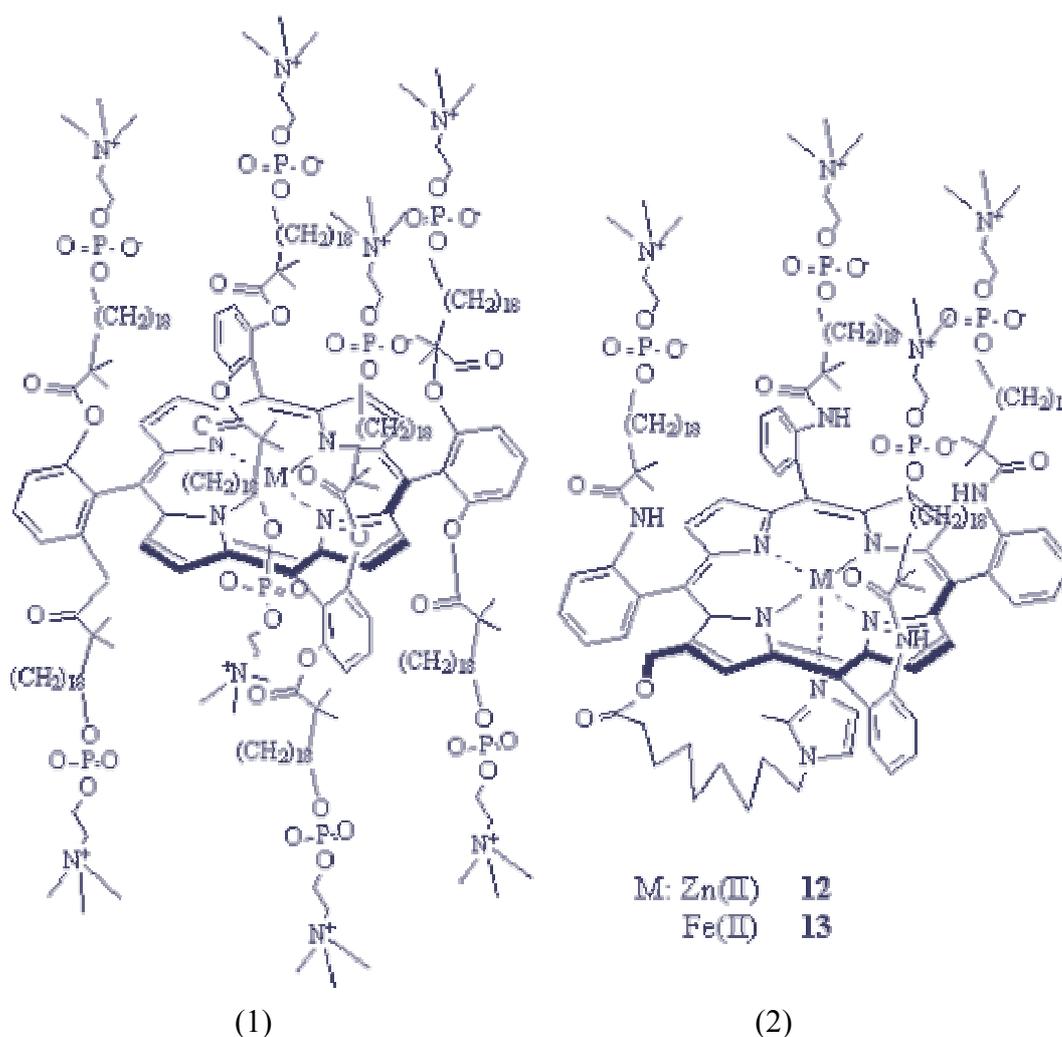


Figure 9. The structure of (1) octopus and (2) lipidporphyrin

6. CONCLUSIONS

Some properties of these organometallic amphiphiles, such as selective binding to metal ions, active control of interfacial tension and catalytic behavior, are present in this article. However, the unique properties of this kind of compounds are far more than those noted, if considered the introduced functional groups. Since the beginning of 90s, organometallic amphiphiles have been becoming more and more accessible. Functionality of increasing complexity has gradually be introduced, leading to their organized assemblies displaying novel chemical and physical properties in relation with coordination chemistry, electrochemistry and molecular materials. Undoubtly organometallic amphiphiles are gradually becoming a new class of surfactants, and maybe open a new vista of surfactant research.

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