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Skills:
(a) Expert with porphyrin and polyoxometalate chemistry as well as formation of hybrid organic – inorganic chromophore(s) – polyoxometalate complexes. (b) Expert with photocatalysis and electrocatalysis. (c) Expert with the electrochemical techniques: coulometry - and exhaustive electrochemical synthesis (preparative electrochemistry) - polarography, spectroelectrochemistry, cyclic and stationary voltammetry, etc… (d) Expert with purification, characterization and studies of organic and inorganic compounds (UV-vis, IR, Fluorescence, photochemistry and paramagnetic and diamagnetic NMR techniques). (e) Familiar with ESR, photochemical and magnetic studies. (f) Teaching undergraduate courses in electrochemistry and general chemistry.

Research:
The main goal of my research developed at the Chemical Physics Laboratory is to obtain organic hybrids of polyoxometalates (POMs) and porphyrins — molecules as well as polymeric materials — able to photocatalytically reduce metal cations or NOx. In these hybrid systems, the porphyrin sub-units will be used as photosensitizers capable of delivering electrons to the strongly oxidant POMs under light irradiation. The reduced POMs can then catalyze reductions, e. g. the reduction of the NOx or of the heavy metal cations Mn+. The porphyrins can be regenerated in the presence of a sacrificial electron donor.

- Our first objective is to prepare and characterize POM-porphyrin model compounds helping understand and predict the characteristics required for good photocatalytic properties. Several types of POM/porphyrin have been introduced (Figure 1).
The second objective is the formation of electrostatic porphyrins/POM complexes in solution from tetracationic porphyrin and polyanion (Scheme 1).

Then, visible light-induced reduction of metal cations such as Ag(I) (Figure 2), Hg (II), Cd (II), Cr (VI), As (III/V)), as well as noble metals with limited resources (Au(III), Pd(II), Pt(II)...), and NOx under aerobic and anaerobic conditions is pursued.

The main rationale for using these porphyrin(s) - polyoxometalate complexes is the possibility to carry out photocatalysis with visible radiation, contrary to polyoxometalates only. Indeed, porphyrins are photosensitizers capable of giving electrons to polyoxometalates after excitation, both through space and through bonds. The complexes are especially attractive, because photocatalysis could proceed with solar radiation.
Previous experiments conducted using electrostatic porphyrins/POM complexes in solution, have already given a positive outcome. Indeed, the electrostatic complexes obtained using tetracationic porphyrins and polyoxometalate have shown a high efficiency toward the model reaction of photocatalytic reduction of Ag(I) even under aerobic conditions. The catalyst was stable under turnover conditions, which is an important criterion for this type of catalysis and bodes well for future applications. Ag (I) was chosen as a model system because it involves the exchange of a single electron. Thus, the photoexcitation of porphyrin units of the complex in the presence of propan-2-ol (sacrificial donor) allowed the catalysis of Ag(I) reduction in Agn.

The mechanism proposed for silver nanoparticle formation corresponds to a direct intramolecular electron transfer from the excited porphyrins to polyoxometalate (Figure 2). Then, the reduced POM – porphyrins complex can transfer electrons to silver ions. The mechanism is similar to that reported for the POM alone excited in the UV domain.

Indeed, the preliminary results shows the efficient photocatalytic reduction of Ag+ in the presence of the complex [ZnTMPyP4+]4[Na2FeIII2(H2O)(P2W15O56)2] using propan-2-ol as sacrificial donor both in aerated and deaerated aqueous solutions (Figure 3). The formed silver nanoparticles are stable in air without illumination.

Figure 3. TEM micrograph of the formed silver nanoparticles and change in the UV–visible absorption spectrum after illumination of aqueous solution containing A) [Co4(H2O)2(P2W15O56)2]16− (0.8.10−5 M) et [ZnTMePyP]4+ (3.2.10−3 M) in the presence of sacrificial donor propan-2-ol (0.13 M) and Ag+ (3.2.10−4 M). Aerated aqueous solution. B) [Co4(H2O)2(P2W15O56)2]16− (0.8.10−5 M) in the presence of propan-2-ol (0.13 M) and Ag+ (1.28.10−4 M). Deaerated aqueous solution.

- The third objective is the formation of supported tetracationic porphyrins – POM.

First, tetracationic porphyrins – POM multilayers were formed. The formation of photocatalysts supported with tetracationic porphyrins and polyoxometalates has been developed using [ZnTMePyP]4+ or (py)ZnOEP(py)4+ in the presence of polyoxometalates in varied structures (Keggin or Dawson). More complex structures of the type sandwiches [M4(H2O)2(P2W15O56)2]16+/12− (where M = Zn2+, Cd2+, Cu2+, Ni2+, Co2+, Mn2+, Fe3+) have also been used.

The feasibility of this approach has been assessed by dipping a glass plate or a transparent electrode of ITO (Indium Tin Oxide) in a alternated way, in a solution 0.5 mM of [ZnTMePyP]4+ and in a solution 0.5 mM of [Co4(H2O)2(P2W15O56)2]16+. Stable multilayers were formed (Figure 4).
Figure 4. Left: UV-visible absorption spectra of [ZnTMePyP^4+ / Co_4(H_2O)_2(P_2W_15O_56)_2]^16_1n films (onto quartz) with different numbers of deposition cycles (after porphyrin and POM depositions). (The measured absorption corresponds to the deposition of material on both sides of the quartz). Inset: Plots of the absorbance at 452 nm as a function of the number n of deposition cycles of [ZnTMePyP^4+ / Co_4(H_2O)_2(P_2W_15O_56)_2]^16_1n in pure aqueous solution. Middle: quartz slide with 25 with different numbers of deposition cycles. Right: TEM images of the silver nanowires with the [ZnTMePyP^4+ / Co_4(H_2O)_2(P_2W_15O_56)_2]^16_1n film in desaerated solutions.

The photocatalytic reduction of AgI_2SO_4 under visible irradiation in the presence of propan-2-ol worked out well. It led to the formation of metallic Ag^0 nanowires (Figure 5).

Second, our previous results showed that a supported catalyst, the cationic copolymer of porphyrins can be prepared by electropolymerization of the bisubstituted monomer 5,10-ZnOEP-meso-(bpy)_2^2+ (1-Zn, Figure 5) via successive scannings between 0.9 V and 1.9 V / SCE leading to the formation of directed nanostructures. Then, the "cationic" electrodes have been soaked in a POM solution to generate a new material.

Figure 5. AFM a) of the copolymer 1-poly-Zn, and b) of the modified electrode dipped 12 hours into a solution of K_4[SiW_12O_40] (c = 1.10^-3 mol.L^-1).

- Our fourth objective is the formation of functional polymers including polyoxometalate.

The key-method for this approach was the electro-copolymerization of hybrid porphyrins developed recently. It is based on the polarization of a working electrode at the porphyrin’s second ring-oxidation potential in the presence of the functionalized POM bearing two pyridyl groups [MnMoxO_{18}((OCH_2)_3CNHCO(4-C_5H_4N))_2]^2- (Py-POM-Py), which generates [POM-porphyrin]_n copolymers after one pot electropolymerization (Figure 4).

The photocatalytic reduction of AgI_2SO_4 or HAuCl_4 under visible irradiation in air in the presence of propa-2-nol at the 2-D interface between water and the copolymeric films worked out well. It led to the formation of metallic Ag^0 nanowires and triangular nanosheets or Au^0 nanosheets (Figure 6).
Figure 6. Electropolymerization of the 5,15-ZnOEP(py)$_2$$^{2+}$ with the Anderson type polyoxometalate Py-POM-Py leading to the copolymer porphyrin – POM. Cyclic voltammograms recorded during the electropolymerization, AFM micrograph, TEM images of nanoparticles obtained after illumination in aerated solution of the copolymer deposited on a plate of quartz in the presence of the sacrificial donor propan-2-ol (0.13 M) and of Ag(I) or Au(III) (1.6 x 10$^{-4}$ M).
EDUCATIONAL BACKGROUND

2011-present: Professor, University of Strasbourg, Laboratory of Electrochemistry, Institute of Chemistry (UMR 7177).
“Electrosynthesis of porphyrin”, “Synthesis of polyoxometallate and study of their electrocatalytical properties” and “Synthesis and study of the catalytic behaviour of new hybrid system polyoxometallate – porphyrin(s)”

1998-2011: Associate Professor, Université Paris-Sud, Chemical Physics Laboratory.
“Electrosynthesis of porphyrin”, “Synthesis of polyoxometallate and study of their electrocatalytical properties” and “Synthesis and study of the catalytic behaviour of new hybrid system polyoxometallate – porphyrin(s)”

- Synthesis of various models, in solution or incorporated in the membrane system, for the biomimetism of the PS II.
- Study of this model with: electrochemistry, spectroelectrochemistry, EPR, and photochemistry.


HDR (Capacitating to steer researches)


THESIS


PUBLICATIONS


7
11 - 2
22+

P. Hapiot - 2
22-
Bis - 2
23
22-

I. Lampre


CHAPTER OF BOOK


PROCEEDING

[1] S. Favette, C. Allain, B. Hasenknopf, **L. Ruhlmann**, « Polyoxometalates as molecular building blocks. » ACS Meeting, Division of Polymer Chemistry, Boston (USA), August 19-23, **2007**. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) 48(2), 663-664 **2007**.

*Covers of journal*