Modulation of the organic heterojunctions behavior, from electrografting to enhanced sensing properties

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The energy barrier of an original organic heterojunction, called MSDI, built on ITO electrodes and combining a low conductive sublayer ($Cu(F_{16}Pc)$) and a highly conductive semiconductor ($LuPc_2$) was modulated by electrografting of organic layers. Impedance spectroscopy clearly demonstrated the increase of the energy barrier at the ITO – sublayer interface. The transport properties of a $LuPc_2$ resistor was totally modified as well. Starting from diazonium salts, we study the grafting of four different aromatic moieties bearing electron-donating and electron-withdrawing substituents. One important feature is that the sensing properties are highly improved compared to the unmodified devices. Thus, the electrografting of dimethoxybenzene doubles the relative response of the heterojunction towards 90 ppm NH_3, as well as the sensitivity in the range 1-9 ppm. This electrografting allows attaining a limit of detection as good as 140 ppb. Sensors operate at room temperature and in a broad relative humidity range. Additionally, the electrografting is a versatile and promising method for the fabrication of symmetrical and unsymmetrical heterojunctions. Finally, it could be used to tune the performances of other conductometric transducers.
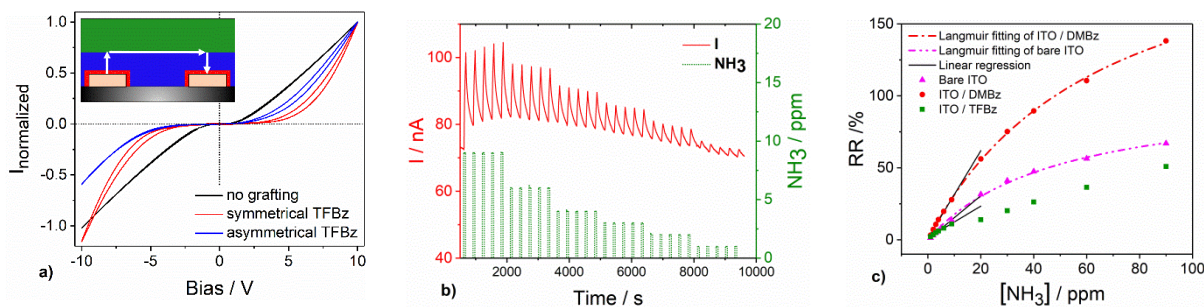
Figure. a) Current-voltage characteristics normalized by the maximum current at + 10 V of an unmodified n-MSDI $Cu(F_{16}Pc)$ – $LuPc_2$ on unmodified IDEs (black) and IDEs modified by symmetrical (red) and asymmetric (blue) grafting of TFBz; b) response of a sensor at low concentrations of ammonia (1-9 ppm) and at 50% rh; c) relative responses RR of the three n-MSDIs in the range 1 - 90 ppm NH_3, at 50% rh.

Molecularly imprinted polymers for the design of electrochemical or fluorescent sensors

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Molecularly imprinted polymers (MIPs) are synthetic polymers mimicking antibodies to selectively recognize a template species (small molecule, protein or ion). Combined with various transduction mechanisms, they are the key stones of a large panel of chemical sensors (optical, electrochemical, QCM) thanks to their high recognition properties, easy synthesis and high stability.[1] A significant improvement of the sensors performances can be reached when the functional monomer, used to prepare the MIP, also acts as a sensing element.[2]

In order to design electrochemical sensors whose functioning is independent of the redox properties of the target species, we have developed the concept of electrochemical MIPs (e-MIPs).[3] This new generation of MIP includes, as functional comonomer, a redox monomer whose modification of the signal during the binding of the target is responsible for its detection. This concept was first validated for the electrochemical quantification of benzo(a)pyrene[4,5] and was further extended to the detection of Bisphenol A pollutant.[6] A limit of detection of 13 ng/L was reached in that case by introducing the MIPs as sensitive and active part of screen-printed electrodes.

In parallel, we designed an innovative fluorescent monomer sensitive to lead(II) ions, which was further incorporated inside ion imprinted polymers (IIPs). The detection of this toxic metal is based on the generation of a fluorescent signal via a photoinduced electron transfer OFF-ON mechanism upon lead binding by the IIP.

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Suitability of metallophthalocyanines MPc as sensitive molecular materials for the development of sensor-systems dedicated to gaseous pollutants monitoring

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With the possibility to modulate the central metal atom and/or to change peripheral groups, metallophthalocyanines constitute a great family of molecular materials appropriate for many applications: dyeing, medicine, electrophotography, organic electronic, solar cell, sensors. Metallophthalocyanine layers can be easily performed on various substrates by soft, inexpensive and industrial methods. Especially in the gas sensors field, the modulation of their physical or chemical properties by adsorbed gaseous species are exploited in electrochemical, optical, acoustic or resistive microsensors. The selectivity to one pollutant can be increased by the relevant selection of transducer.

Adsorption of oxidizing gases leading up to high conductivity variations of metallophthalocyanines, resistive microsensors involving copper phthalocyanine as sensitive material are highly relevant for NO_2 and O_3 monitoring, even at ppb level. As complementary, because of the high adsorption of aromatic hydrocarbons on tert-butyl phthalocyanines, quartz crystal microbalance coated with such materials exhibit a great sensitivity to BTEX pollutants. Sensing layer characterizations by SEM, AFM and XRD have highlighted the key role of layer morphology at molecular scale on sensing performances. The influences of layer thickness, the nature of central metal atom and the electroactivity of the peripheral ligands on sensor responses have been investigated. The advantages of nanocarbons functionalization by metallophthalocyanines for sensor applications have been also established. Metrological performances of such microsensors especially aiming to air quality monitoring will be discussed from experimental results performed in laboratory as well as in real conditions.

Carbon nanotube based toxic gas sensor : Improved sensitivity and selectivity using molecular/polymeric selectors

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Portable and low cost chemical sensors enable personal monitoring and sharing information on hazardous chemical substances, which are of increasing interest for security, occupational safety, and health. In this talk, single-walled carbon nanotube (SWCNT) based electro-chemical sensor that can detect ppm-level toxic gas will be presented.

SWCNT wrapped with metallo-supramolecular polymer (MSP) demonstrates amplified and time-integrated increase in electrical conductivity when disassembly of MSP is triggered by electrophilic chemical substances including diethyl chlorophosphate (DCP), a nerve agent simulant [1, 2]. SWCNT-MSP composite material demonstrate over 3000% increase of electronic conductivity upon cumulative exposure to sub-ppm order of DCP (Fig. 1a). Owing to an enormous sensing response, our material is compatible with a wireless sensing system based on near field communication (NFC) technology. Thus, commercial smartphone can be employed for facile detection of harmful vapors (Fig. 1c).

Besides, chemiresistive-sensor consisting of SWCNTs and hydroxylamine hydrochloride enable highly selective and continuous monitoring of formaldehyde [3]. The SWCNT sensor is reusable in air; has a detection limit of 0.016 ppm; HCHO-selectivity of 10^5 to 10^6 times higher than other vapors such as water and methanol (Fig. 1b).
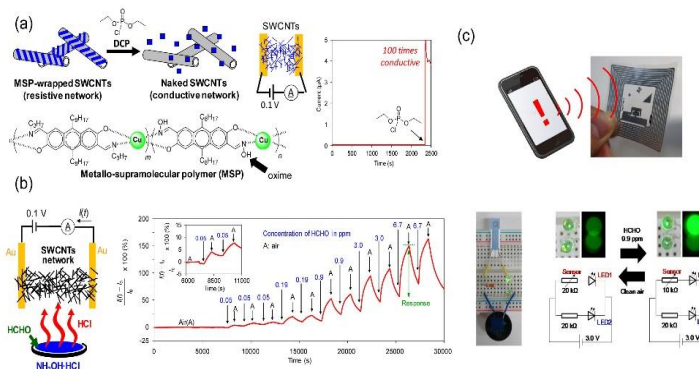

Fig. 1 (a) Detection of nerve agent simulant using SWCNT-based sensor. (b) Detection of formaldehyde using SWCNT-based sensor. (c) Examples of simple devices.

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Synergistic effect of polyoxometalate and single walled carbon nanotubes on peroxidase-like mimics and highly sensitive electrochemical detection of hydrogen peroxide and of glucose

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Keggin type POMs ($XM_{12}O_{40}^{n-}$, X = P, Si/M = W, Mo, V). offer favorable accessibility for electron transfer from empty d orbitals for metal–oxygen π bonding. They can undergo a stepwise multielectron reversible redox process without any structural changes. In this study, a new organic-inorganic material, based on an alpha-metatungstate $[H_2W_{12}O_{40}]^{6-}$ cluster, was synthesized via the hydrothermal method by using aminopyridinium $(APy)^+$ cations as the hybrid material, and characterized by FT-IR spectrometry and thermal analysis. A simple and reliable procedure was implemented for the synthesis of new composite materials obtained by the covalent grafting of $(APy)_6[H_2W_{12}O_{40}]$ onto the surface of carboxylic acid functionalized single-walled carbon nanotube (SWCNT-COOH). The synergistic effect of single-walled carbon nanotubes on the electrochemical behavior of $(APy)_6[H_2W_{12}O_{40}]$ was evidenced through the negative shift of the reduction peaks and their increased intensities - several times higher- which must be due to the energy level stabilization of $(APy)_6[H_2W_{12}O_{40}]$ through electron transport from the LUMO orbitals of the SCWNTs to the LUMO orbitals of $H_2W_{12}O_{40}$, as shown on the Figure. The sensitivity of hydrogen peroxide detection was increased by a factor of 38.5 in presence of SWCNT, showing their high influence on peroxidase-like mimics of $(APy)_6[H_2W_{12}O_{40}]$.

$$[H_2W^{VI}_{11}W^VO_{40}]^{7-} + H_2O_2 + 3e^- + 2H^+ \qquad [H_2W^{VI}_{10}W^V_2O_{40}]^{8-} + 2H_2O$$

ELECTRON TRANSFER
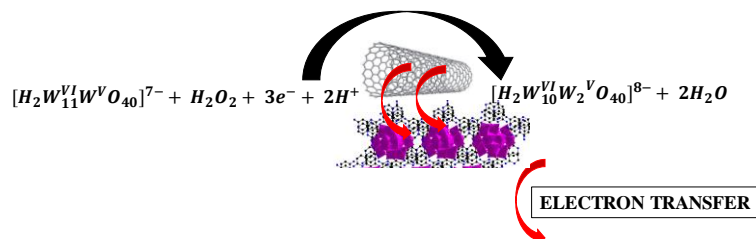
An enzymatic biosensor was fabricated through the immobilization of glucose oxidase (GOx) on the SWCNT-CO-$(APy)_6[H_2W_{12}O_{40}]$ modified gold electrode. A selective glucose biosensor with a detection limit of 2 nM, a large dynamic range up to 10 mM and an operational shelf life of more than two months, was obtained.

Moisture Sensor for supersensitive detection

of dew condensation

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Dew condensation causes various phenomena such as corrosion of metal, fogging of glass and disease to crops. In order to suppress or prevent dew condensation, it should be detected at an initial or early stage. The conventional techniques, however, are useless for that purpose. For instance, when relative humidity (RH) reaches 100%, dew condensation must occur while a common method to estimate RH estimated from changes in electrical resistance or capacitance of hygroscopic polymer by absorption of water vapor in the atmosphere cannot detect occurrence of condensed dew, i.e. liquid water it also takes 10 seconds and more to respond to the changes in RH. On the other hand, most commercial methods of water detection by change in electrical signal between two electrodes are applicable to comparatively much water in visible extent grown by continuous dew condensation. NIMS has developed a sensor that detect fine and slight water with high accuracy and quick response, based on galvanic current generated by attaching water like a bridge between different metal lines with a narrow gap.

The sensor electrodes were interdigit arrayed lines of Au and Al with 1 µm in width and 0.2 µm in thickness were opposed and inserted between mutual lines in a length of 1 mm with gaps of 0.5 to 10 µm on a silicon wafer covered with a silica layer. Electric current from the sensor electrodes was measured at a minimum interval of 0.2 sec through a device for A/D conversion of the signal from the sensor electrode. Humidity around the sensor electrodes controlled from 30% to 100% and the temperature of the sensor was changed from the ambient temperature to dew point. The microscopic observation of the surface of the sensor electrodes was carried out under the control of humidity around the sensor electrodes.

The experimental results showed that current response of the sensor coincided with appearance / disappearance of water droplets on the sensor surface. Furthermore, this sensor detected clearly water droplets under high humidity more than 80 % could be detected, which is difficult to detect with a general hygrometer. In addition, narrower gap between the sensor electrodes showed more sensitive response to smaller water droplet. Especially, the electrode with the gap of 0.5 µm also showed stepwise current response according to the changes in humidity from 60 % to 90 %.

This study summarized this sensor could detect dew condensation at an initial or early stage and be used for sensing of moisture in the environment.

Innovative organic dielectric/semiconductor interface: Application to ISFET sensors for the detection of Cesium

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The development of sensors with low limit of detection and a specificity that can be easily tuned is still a challenge in the field of sensors. We present an original platform constituted of an engineered lipid monolayer which is used as the active sensitive layer and as ultra-thin gate dielectric in field effect transistor sensors. Supported lipid layers, with thicknesses of a few nanometers indeed constitute good candidates. In living cells lipid membranes are known to constitute natural insulators which play an efficient role as barrier to both ionic and electronic transport across the membrane, associated with an electrical resistance of the order of several giga-Ohms in magnitude. However, despite excellent insulating properties, lipid bilayers and even more lipid monolayers have been poorly exploited in devices due to their inherent instability under application of an electric field, leading to damages caused mainly by an electroporation process occurring at low electric field. Furthermore, a lack of mechanical stability is often observed.

We show that the mechanical and chemical stability of lipid layers as well as their dielectric performances can be improved by changing the molecular structure of the lipids and by achieving intra-chain reticulations within the layer, and that surprisingly both these properties are correlated. In fact such reticulated layers with a thickness of 2.5 nm only have a direct dielectric breakdown occurring at ~30 MV/cm, i.e. much higher than for a silicon oxide layer of similar thickness.

We show that ones the lipid monolayer on the transistor channel the specificity of the sensor given by the grafting of probes to the lipids can be tuned using simple procedure making our sensor extremely versatile.

As a proof of concept, we present here a lipid based sensor that was developed for the detection of Cs^+ ions using organic transistor with a poly(3-hexyl)thiophen (**P3HT**) as channel and calixarene as probe.

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Nanoscale Electrochemical Imaging on Electrode Functional Materials by Scanning Electrochemical Cell Microscopy

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Recent progress of electrochemical based energy harvesting or storing electrode materials are remarkable. In particular, a precise size control with nano-/atomic level of those materials is essential to enhance their electrochemical activities. In general, to evaluate their electrochemical properties, a conventional analytical technique is conducted in bulk states. In other words, there is a still major issue to understand their local electrochemical properties such as ion transport in lithium-ion batteries and electrocatalytic reactions. In comparison with *electronic* conduction analysis by scanning probe microscopies such as scanning tunneling microscopy, it is still required to develop a spatially resolved electrochemical analysis with high sensitivity in *ionic* conduction. To overcome it, we have worked on variety of electrochemical microscopies. In this talk, we will introduce a self-assembled scanning electrochemical cell microscopy with a single barrel nanopipette (SECCM) for visualizing electrochemical reaction (i.e. nanoscale electrochemical imaging) [1]. The size controllable pipette (e.g. 50 nm) is filled with electrolyte and a quasi-counter/reference electrode, which is specialized to detect ionic current though a meniscus created between the pipette and sample surface. The SECCM can utilize in any electrochemical activities. For battery analysis, it can be applicable to investigate local lithium ion activities on electrodes [2]. Further, hydrogen evolution reaction on two dimensional materials such as graphene is visualized [3].

Scanning Electrochemical Cell Microscopy

Nanoscale Electrochemical Imaging
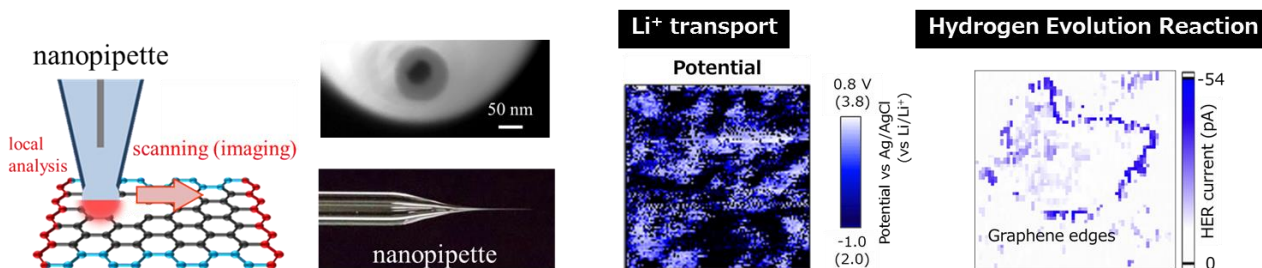
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Multi-responsive porphyrins for sensing applications

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ABSTRACT

Porphyrins are widely studied functional dyes that play essential role in living organisms (e.g. photosynthetic antenna and reaction center, heme protein as an oxygen carrier, etc.). Previously, we have shown that porphyrins can be used for various sensing applications[1-8] such as enantiopurity detection, selective detection of anions, determination of trace water impurities in organic solvents, etc. However, most of these properties are achievable only in organic solvents (chloroform, DMSO, etc.). Therefore, we have synthesized water soluble porphyrin derivatives (Fig. 1a), which also exhibit reversible response to various external stimuli such as temperature (phase separation, Fig. 1b), pH (colorimetric response, Fig. 1c) and solvent composition (co-nonsolvency, Fig. 1d). We attempt to describe this rich behavior using various concepts of physical chemistry, such as chemical equilibria, chemical kinetics and Flory-Huggins solution theory. Potential applications of these effects, such as photodynamic therapy (PDT) or magnetic resonance imaging (MRI) imaging of chirality will be also discussed in the presentation.
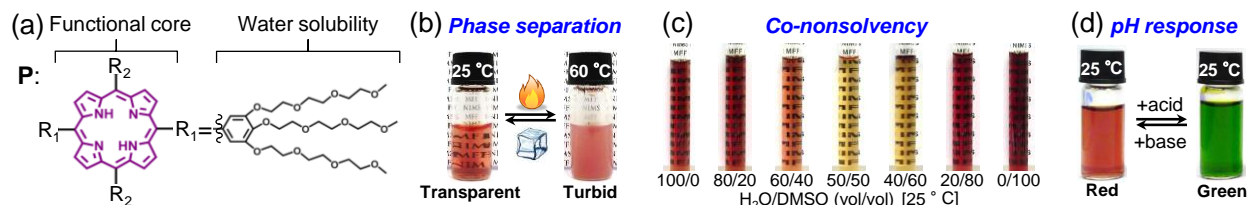
Fig. 1. (a) Structure of water-soluble porphyrins (P). (b) Phase separation. (c) Reversible pH response. (d) Solvent composition response (co-nonsolvency).

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Functional materials involved in opto-electronic devices for gas sensor, photodetectors and photovoltaic conversion.

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Functional materials, constituting organic, inorganic or hybrid components, are considered potential platforms for applications in extremely diverse fields such as optics, micro-electronics, health, energy, energy storage, diagnosis and environment. Material properties of such materials can be tuned by modification of the composition on the atomic or molecular scale to be involved as active materials in operational and smart devices defined as sensors. Furthermore, the fabrication of optoelectronic devices via spin-coating onto a pre-selected substrate offers ease of integration, low cost, and physical flexibility. Both metal-oxide-semiconductors and organic semiconductors have been considered as promising candidates for either gas or optical sensors.

Over the past few years, metal-oxide-semiconductors as a class of chemiresistive sensors have attracted great attention in environmental monitoring, automotive emission monitoring and food safety testing, due to their low production cost, high sensitivity, simplicity of use and their ability to detect various gases. We present here the efficiency of metal-oxide-semiconductors as zinc oxide nanoparticles (ZnO), new synthesized doped ZnO nanoparticles (Aluminum-doped ZnO) and tungsten trioxide nanowires (WO_3, Ag-WO_3), deposited on substrate by solution process (drop coating, spin-coating) from colloidal solutions [1]. The sensing properties of metal-oxide-semiconductors exposed to different gases (O_3, NO_2, NH_3) not only depend on the morphological structure (particle size, morphology, pore size, etc.), but also rely on the defect structure and heterointerface structure (grain boundaries, interfaces, defect concentrations). This observation was also confirmed by transport studies on thin-film films in organic thin film transistors (OTFTs) [2]. As optical sensors, we fabricated and characterized organic semiconductor-based devices as organic photovoltaics (OPVs) and organic photodetectors (OPDs) where such organic materials have revealed remarkable prospective for use in optical to electrical conversion applications. The efficiency has be strongly improved over the past few years thanks to intensive development of new materials process photoactive layers as well as interfacial layers (IL) and novel device structures [3-4].

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