POSTERS SESSIONS

Tuesday 18 December, 10:00 – 11:00
15:50 – 16:50
Electro-Optical and thermophysical characterization of composite materials based on polymers and liquid crystals

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Abstract:
This work examines the development and characterization of TPGDA / E7 mixtures of the PDLCs type. These systems are produced by UV irradiation photopolymerization (PIPS) of a mixture of monomers tripropylene glycol di-acrylate (TPGDA) and the liquid crystal E7, in the presence of the Lucirin TPO photoinitiator. An electro-optical, thermal and optical characterization is invested in order to understand the effect of CL concentration on the electro-optical and thermo-physical properties of these materials. Polarizing optical microscopy (POM) and differential scanning analysis (DSC) studies were performed so as to determine the transition temperatures of these materials in accordance with the composition of these systems. The findings show a slight variation of the nematic-isotropic transition temperature $T_NI$ of LC E7 and of the glass transition temperature $T_g$ of the TPGDA polymeric matrix, as a function of the mass percentage of CL E7. A very good electro-optical response for the composition 30/70 Wt.% in LC E7 was obtained.

References:
Bidirectional Multiple Negative Differential Resistance (NDR): An Interplay Between Interface Resistance and Redox Reaction

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Abstract:

Multiple negative differential resistance (NDR) was observed on both the directions of the voltage window from a single 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) molecule when the device was studied by using density functional theory (DFT) in association with non-equilibrium Green’s function (NEGF). The carrier transport in the device occurs mainly through the transmission channel corresponding to the highest occupied molecular orbital (HOMO) of the molecule and a commensurate change in the magnitude of transmission peak was observed at the peak and valley voltages. The reason for the NDR is proposed to be due to the two competing factors involved namely, the reduction of the molecule and the interface resistance between the molecule and the electrodes. The involvement of both the factors is validated from the molecular projected self-consistent Hamiltonian (MPSH) and the local device density of states (LDDOS) of the device at the corresponding peak and valley voltages.

Figure 1. The I-V characteristic curve for the device taken between -2.5 to 2.5 V, but here the range is shown from -2 to 2 V.

Figure 2. (a) and (b) represent the eigen states of MPSH for the positive and the negative peak and valley voltages. The peak and valley voltages in the positive side are 0.18 V, 0.84 V, 1.66 V and 0.39 V, 1.42 V, 2.15 V respectively. Similarly, for the negative side the peak and valley voltages are -0.20 V, -0.77 V, -1.46 V and -0.44 V, -0.13 V, -2.10 V respectively.

Reference:

Highly reproducible formation of polymer single-molecule junction for well-defined current signal

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Abstract:

Single-molecule devices attract much interest to develop nanoscale electronics. Although a variety of functional single molecule for single-molecule electronics have been developed, there still remain needs to implement sophisticated functionalization of the devices toward practical applications. Given its superior functionality encountered in macroscopic materials, polymer could be a useful building block in the single-molecule devices. Here, we created molecular junction composed of polymer. We found that the polymer junction exhibits the higher formation probability and the longer lifetime than its monomer counterpart, demonstrating that polymer provides unique opportunity to design both stable and highly functional molecular devices for nanoelectronics.

The tunneling current was measured by STM for an Au(111) surface modified by poly-vinylpyridine (PVP; Figure (a), bottom) or its monomer counterpart, tri-methylene-di-pyridine (TMDP; Figure (a), top). The spontaneous formation of the molecular junction was investigated using STM I-t measurement. In the I-t measurement, the tunneling current was recorded as a function of time at a fixed tip-substrate distance. The formation of the molecular junction was evident by the current increase and consecutive plateau (Figure (b)). We developed an automated algorithm for the precise detection of these current plateaus and evaluated the properties of individual molecular junctions.

The analysis revealed that the polymer junction exhibits the higher formation probability and the longer lifetime than its monomer counterpart (Figure (c,d)). Based on the XPS analysis, the higher formation probability of polymer junction was attributed to the presence of unbound pyridine linkers, which facilitate the formation of the molecular junction. The longer lifetime of PVP reflected the robustness of the polymer adsorption structure, originating from the multidentate effect. These results suggest that polymer provides useful perspectives to design both stable and highly functional single-molecule devices for nanoelectronics.

Figure

(a) The chemical structures of TMDP and PVP. (b) Typical I-t traces measured with TMDP- and PVP-modified substrates. Bar graphs showing (c) formation probabilities and (d) lifetime of TMDP and PVP molecular junctions.
New way to rectify current thanks to Ferrocenyl Triazole derivatives

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Abstract:
Rectification of current by molecules is a subject that attracts many attentions nowadays because it would permit to reduce the size of the electronic devices. Theorized by Aviram and Ratner, the rectification can be achieved by an asymmetric molecule, enabling the electrons to be transferred in a preferential direction through the molecule. The state of the art of the organic molecular rectifiers shows rectification ratios up to $10^5$. [1] Such rectification ratios were obtained with molecules composed of a ferrocene, which is the key of the rectification process, linked to an insulating alkyl chain. At present, few studies have been devoted to control the orientation of the molecular rectifiers, relative to the electrode. More precisely, the possibility to anchor the molecular rectifier to the two electrodes while controlling the orientation has only been scarcely investigated. In our case, such a control of the molecular orientation has been obtained by developing a two-step process based on Click Chemistry.

Figure: Importance of position of ferrocene in the rectification

Here, we present unprecedented works on the synthesis of new ferrocene derivatives designed as molecular rectifiers. Especially, a special effort is devoted: firstly, to allow the molecule to be covalently linked to an electrode and secondly to definitely control the orientation of the molecular rectifier relative to the electrode.

References:
Random Telegraph Signal and Single Charge Trap Dynamics Investigated with Graphene Tunnel Junctions

Pawel Puczkarski, Qingqing Wu, Hatef Sadeghi, Songjun Hou, Amin Karimi, Yuewen Sheng, Jamie H. Warner, Colin Lambert, G. Andrew D. Briggs, Jan A. Mol

Abstract:
Graphene Tunnel Junctions (GTJs) have already been proven to be a facile experimental platform for measurements of electronic properties of single molecules. Such devices, formed by feedback-controlled electroburning, are advantageous because of the feasibility of controlling the inter-electrode distance with sub-nanometre precision, the possibility of the covalent and non-covalent functionalization of graphene with molecules, and their higher gate coupling compared to metal-based junctions. In addition to single-molecule experiments, there is the prospect of exploiting GTJs for other applications, such as the investigation of thermoelectric effects or biosensing and in particular sequencing of DNA strands, protein chains and linear carbohydrates.

The performance of GTJs applied to molecular electronics and biosensing is strongly dependent on the noise characteristics of the devices. Here, we report on the first comprehensive study of the noise properties of GTJs. The investigation of noise in GTJs at room temperatures reveals a flicker noise spectrum, typical to diverse electronic systems. The origin of this flicker noise spectrum can be attributed to the superposition of multiple two-level switching random telegraph signals (RTSs) with a distribution of characteristic dwell times. We confirm this by the observation of RTSs and corresponding Lorentzian noise spectra in GTJs characterized at cryogenic temperatures. By means of electrostatic considerations and simple tight-binding model used to model transport through a GTJ we conclude that the observed switching behaviour can be attributed to the shift of a tunnel barrier induced by electrostatic field of a single electron, switching between two adjacent charge traps, present in the underlying silicon oxide substrate in the vicinity of the GTJ. Further statistical analysis of switching signals demonstrates that the devices can provide insight into trap interactions, showing effects related to the Coulombic intertrap repulsion. This indicates high sensitivity of GTJs to their electrostatic environment, a feature that can be harnessed in GTJ biosensing protocols.

Figure 1. Features of A) RTS and B) Lorentzian noise spectrum observed in tunnelling current measured in a GTJ at 77K. Red line in Figure B) shows fit to noise model consisting of a superposition of flicker, Lorentzian and white noise spectra.

References:
Understanding electronic transport through porphyrin-based molecules

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Abstract:

Porphyrin-based molecules have a great potential in molecular electronics as their electronic properties can be easily tuned by modifying their chemical structure [1]. Hereby, they offer an interesting platform to understand charge transport through single molecule devices.

In this study, we have tested several Porphyrin-based molecules with different central elements and anchoring groups. The measurements were performed using the Mechanically Controllable Break-Junction (MCBJ) technique at room temperature. Using this technique, we acquire statistics of the conductance properties by recording thousands of traces.

To identify the different electronic configurations of the molecules and their conductance signature, we used a custom clustering method to sort the current-displacement traces. Several classes were identified and can be used in the future to gain more insight on the electronic pathways.

References:

Ligand-field-modulated molecular rectifiers: on the junctions of acetylene-gold electrodes

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Abstract:
The quest for a mechanism facilitating the rational design of molecular rectifiers is among the major challenges of molecular electronics. Demonstrated by acetylene–gold bonding in this presentation, we introduce the concept of ligand-field theory1 to single-molecule junctions. With the formation of C–Au bond2 at the under-coordinated gold atom of the electrode apex, the electrostatic field of −C≡C: drives the hybridized C–Au orbitals shifting towards $E_{\text{Fermi}}$ and improve the degree of energy-level alignment at the molecular junction (left panel of Figure b). Transmission spectra (QuantumATK) of a series of applied voltages (Figure a) show that the HOMO band is reached by the bias window at +1.2V but not at the opposite bias of −1.2V, indicative of the characteristics of rectification. The strength of ligand fields is examined by ligands (e.g., −C≡CN and −S(CH₃)₃) and electrode geometries (flat and pyramidal). The splitting magnitudes between the bonding and antibonding orbitals and the corresponding simulated $i-V_{\text{bias}}$ curves will be reported. This work presents ligand-field theory-based molecular rectifiers and validates a new approach to design functional molecular devices.

Figure a, $V_{\text{bias}}$-dependent transmission spectra of Au-NC-(C₆H₄)-CC-(C₆H₄)-CC-Aupyramidal junctions. The purple triangles illustrate the windows of the applied bias voltages. Note that, upon the increase of $V_{\text{bias}}$, the peak position of HOMO shifts toward $E_{\text{Fermi}}$. b, illustration of the ligand-field theory-based rectification mechanism. In the schemes, the acetylene-gold contact are made at the right electrode where the effect of orbital pinning takes place due to the strong −CC-Au coordination. Right panels depict how orbital pinning leads to rectification. Apparently, a stronger ligand field effect would yield a larger splitting and a smaller on-set voltage.

References:
Designing of a “perfect” porphyrin molecule for the Mechanically Controllable Break Junction Experiments

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Abstract:

The biggest challenge of molecular electronics is to condense the functionality of an electronic device into a single molecule and to exploit the functional versatility offered by the chemical diversity of molecules for electronic device purposes.

Porphyrins and their related macrocycles are promising building blocks for the construction of bio-inspired molecular devices. Nature itself offers magnificent examples of porphyrin usefulness, such as activating and transporting molecular oxygen in mammals and harnessing sunlight in plant photosynthetic systems.

In spite of their potential, obtaining well defined single molecule conductance features is a difficult task. Due to $\pi$-stacking porphyrins can form a variety of junction configuration, leading to large spread in conductance values using the mechanically controllable break junctions (MCBJ) technique\textsuperscript{1,2}. This limit the further progress in investigating the molecular functionalities on a single molecule level in porphyrin molecules.

In this presentation, I will show that by close interaction between synthetic chemists and physicists a “perfect” porphyrin molecular design for mechanically controllable break junctions\textsuperscript{3,4} can be achieved, leading to well defined, highly conducting molecular junctions. This opens further prospects for “porphyrionics” – porphyrin based molecular electronics.

References:


Acknowledgements: This work has been performed in collaboration with prof. van der Zant group at the TU Delft and has been supported by by the EU through a RISE(DAFNEOX) project, SEP 210165479 and FONDECYT Regular Grant 1140770. The author would like to acknowledge synthetic chemistry groups of Marcel Mayor (University of Basel), Jonathan P. Hill (NIMS, Tsukuba, Japan) and Rienk Eelkema (TU Delft) who provided molecules for these studies.
Charge transport through graphene based molecular junctions

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Abstract:
Understanding charge transport at the level of a single molecule is of great importance for both fundamental research and applications in electronic devices. Due to its electronic and mechanical properties, graphene offers a stable and gateable platform to study charge transport through molecules. However, to realize reliable graphene-based junctions, several issues still need to be addressed. First, graphene-based junctions have been reported to exhibit signatures similar to these of molecules, with gate-dependent resonance features [1,2]. Secondly, connecting molecules to the graphene remains challenging as achieving at the same time mechanical stability and electrical reproducibility is not straightforward. Both impose different requirements on the junction properties and finding the proper balance between electronic and mechanical stability is therefore challenging. Third, the silicon dioxide substrate has been reported to yield feature-rich charge-transport characteristics, primarily due to switching within the oxide [3].

In this study, we report on the realization of a mechanically and electronically robust graphene-based multi-molecule junction [4]. The mechanical stability is achieved by anchoring molecules directly to the substrate using silanization, rather than to graphene electrodes. The electronic stability, on the other hand, is due to a large overlap of the π-systems of neighboring head groups. The nature of the stacking also renders it less sensitive to the electrode properties. The junctions are reproducible throughout several devices and operate up to room temperature. Our approach allows for the future integration of novel molecule based functions into stable and controllable nano-electronic devices.

References:
Single-Molecular Conductance in the Junction of Electrodeposition-Modified Electrodes

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Abstract:

The electrode-headgroup coupling plays an important role in the contact resistance/electrical performance of single-molecular devices. Minimizing the contact resistance is one of major tasks to reduce the unwanted voltage loss across the molecular junction. To achieve superior electrode-headgroup contact, ideal anchoring groups are those exhibiting reasonable affinity to the electrode. For example, the sulphur-gold contact is popular but the carboxylate-gold contact is not, due to the difference in the strength of adsorption. Alternatively, carboxylate-terminated molecules are known to interact strongly with silver which, however, bears native oxides under ambient conditions and is prone to contamination. Such drawback associated with the oxide layer is circumvented by an electrochemical phenomenon termed underpotential deposition (UPD) that only a monolayer or submonolayer of foreign metal is deposited at a potential positive from the Nernst potential of the bulk reduction. Our previous XPS (x-ray photoelectron spectroscopy) study demonstrated that UPD-modified surface was oxide-free yet exhibited affinity toward carboxylate. Herein, we employ Ag-UPD-modified Au electrodes to measure single-molecule conductance of carboxylate-terminated molecules. To conserve the Ag monolayer, a non-destructive methodology (atomic force microscope) developed by Chen etc. instead of conventional break-junction techniques was employed. By keeping constant the force between the molecule and the AFM tip, the lifetime of the junctions can be maintained for longer than 150 sec. which enables (1) reducing the times of fusing together and breaking apart between two electrodes and (2) the measurements of i-V curves from the same junction. In this presentation, we will show that, with UPD-modified electrodes, the junctions of alkanedicarboxylic acids have the better electrical and mechanical properties than bulk Au electrodes. Furthermore, Au electrodes modified by other UPD metals such as copper and bismuth also exhibit enhanced coupling and contact conductance for carboxylic anchoring group.

References:

Environment-Dependent Electron Transfer in Single-Porphyrin Transistors

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Abstract:
Electron-transfer is central to biological processes and emerging quantum technologies, and is at the core of chemical challenges related to energy conversion. In Nature, electron transfer takes place within well-defined environments, whereas fabricated systems usually feature an uncontrolled solvent shell, or substrate, surrounding the centre of electron transfer. There are gaps in fundamental descriptions of electron transfer at the single-molecule level, and this is reflected in the absence of a model that quantitatively reproduces current-voltage responses in molecular devices. We have studied electron transfer in a single-molecule transistor to test the role of the inner and outer sphere rearrangement of the nuclei. We find that at low temperature (4 K) electron-vibrational coupling leads to fine structure in the charge transport properties; this structure is washed out over 20 K. Our data display a simultaneous breakdown of quantum coherent Landauer and semi-classical Marcus theory at liquid nitrogen temperature. We find that quantum mechanical nuclear tunnelling enhances low-energy electron transfer rates, and our experimental results can be reproduced quantitatively using a quantum master equation model.\cite{1} The combination of our experiment and theory shows that electron transfer at the quantum-classical boundary is extremely sensitive to the outer sphere reorganisation. The impact of the environment cannot be neglected in the development of single-molecule devices.

Figure 1: (a) Schematic of our device architecture\cite{2}. Molecule M, shown in (b), spans nanometer-spaced graphene electrodes. (c) Charge stability diagram as a function of bias and gate voltages, lines running parallel to the edges of the resonant transport region indicate vibrational excitations accompanying electron transfer. (d) Schematic of current flow through our device at negative source-drain bias, the energy-dependent electron-transfer rates of reduction at the source and oxidation at the drain are shown in red and blue respectively.

References:
Transmission Spectra of Single Molecule Junctions:
Fitting of $i$-$V_{\text{bias}}$ curves acquired under electrochemical control

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Abstract:

Transmission spectra simulate electron transport across electrode-molecule-electrode junctions and facilitate the prediction of the electric performance. To turn the conceptual spectra into measurable quantities receives much attention. Herein, the molecular junctions were integrated in an electrochemical setup. The relative potential of the working electrode ($E_{\text{wk}}$) to those of the frontier orbital levels of the bridged molecule was driven electrochemically to change the degree of the energy-level alignment. $i$-$V_{\text{bias}}$ measurements which conferred transition voltage ($V_t$) was conducted as a function of $E_{\text{wk}}$. Energy offsets ($\epsilon$) between Fermi level of the electrode and that of frontier orbitals were derived from a single-level Landauer fitting. Ambiguity may arise when correlating $V_t$ with $\epsilon$ due to possible contribution from additional resonance levels. Hence, we revisited and discussed the meaning of $V_t$ and the suitability of the single-level Landauer fitting.

References:

Contact Metal Effects on the Conductance of Alkanedithiol Single-Molecule Junctions

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Abstract:

The conductance of pentanethiol (PDT) molecules was assessed using a mechanically controllable break junction (MCBJ) with notched wire samples of cobalt and gold wire. The current through PDT was measured by repeatedly forming break junctions between the two electrodes which had been exposed to a high concentration of PDT in ambient air for 48 hours. Measurements of Au-PDT-Au junctions show a molecular conductance of $\sim 10^{-3} G_0$, a value supported by the literature [1]. Preliminary measurements of the Co-PDT-Co junction indicate that molecular conductance is an order of magnitude higher than for gold $\sim 10^{-2} G_0$. This suggests a difference between the binding mode of the thiol at the metal surface. Such a distinction could arise from a significant role of the Co d band electrons in the thiol linking mechanism. In addition, the measurements of the Co-PDT-Co junction were carried out under ambient conditions without electrochemical control. Hence, it was anticipated that rapid oxidation of the cobalt surface would impede acquisition of high-quality results. The ability to collect good data without electrochemical control is an interesting result. It has previously been suggested that the amount of surface oxide on an oxidised cobalt substrate can be decreased if the exposure time to an alkanedithiol-rich environment is increased [2]. Alternatively, these results may indicate that on formation of a new junction, a cobalt-PDT interaction can occur more quickly than oxidation. Initial results collected using Nickel electrodes agree with the larger conductance value found using cobalt electrodes.

References:


Electronic characteristics in single extended metal-atom chains

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Abstract:
Prototypical EMACs (Extended Metal-Atom Chains) are one-dimensional metal atoms helically coordinated by nitrogen atoms of four α-pyridylamine ligands (Figure 1). The conductance of EMACs can be adjusted by ligand design, the selection of the element used for the metal centers, and the oxidation states of the metal centers. In this poster presentation, we show that [Rh3(dpa)4(CN)2] exhibits an interesting behavior of conductance switching, from a lower conductance level to a higher one when the molecule was subjected to stretching. This is opposite to the findings in most studies of single-molecule conductance where the molecular conductance decreases when the molecules are stretched. Experiments that repeatedly change the molecular lengths by mechanical modulation of the junction size and tune the oxidation states of [Rh3(dpa)4(CN)2] electrochemically suggest that the one-electron oxidized form, [Rh3(dpa)4(CN)2]⁺, adopts a shorter configuration and lower conductance than those of its neutral form, [Rh3(dpa)4(CN)2]⁰. Simulations are underway to correlate the relative energy-level alignment between the electrode Fermi level and the frontier molecular orbitals of the two oxidation states.

Figure 1. The molecular structure of [Rh3(dpa)4(CN)2].

Figure 2. (Left Panel) 2D conductance histogram of [Rh3(dpa)4(CN)2] junction in 1,2,4-trichlorobenzene under a bias of 50 mV. (Middle) 2D histogram exhibiting the behavior of conductance switching. (Right) A sample trace with conductance switching. The numbers of traces for the left and middle panels are 5846 and 311, respectively.

References:
A plasmonic molecular electronic device, consisting of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires bridging an ultramicroelectrode and an indium tin oxide (ITO) substrate covered by gold nanoparticles (Au NPs), has been developed. Light irradiation of this device has a dramatic impact on its conductance. Polymer strands, maintained electrochemically in their oxidized, conducting state, reversibly switch to their insulating state upon irradiation by visible-wavelength light, resulting in a sharp decrease in the conductance. The high-conductance state is restored when the light is turned off. Switching depends on the wavelength and the intensity of the incident light. It is due to reversible reduction of the nanosized region of PEDOT nanowires in contact with a gold NP and is attributed to plasmon-induced hot-electron injection into the PEDOT. The high/low conductance ratio can be as great as 1000, and switching requires low light intensity (220 W/m²). These results could open the way to the design of a new family of optoelectronic switches.

Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature

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\textsuperscript{d) Department of Advanced Materials Science and Nanotechnology, University of Science and Technology of Hanoi (USTH), Vietnam}

Molecular electronics started with the idea that a molecule sandwiched between electrodes may behave as a rectifying device. Since then, a number of studies have been reported that a molecule can rectify. Recently, C.A. Nijhuis et al has reported a SAMs molecular diode with high, robust, rectification ratios of $1.1 \times 10^3$. \cite{1}

In this work thin layers of oligomers with thickness between 7 and 9 nm were deposited on flat gold electrode surfaces by electrochemical reduction of diazonium reagents, then a Ti(2 nm)/Au top contact was applied to complete a solid-state molecular junction. That makes it possible for the direct evaporation of various metals on the grafted organic layer in order to fabricate the top electrode through CMOS processes\cite{2,3}. The influences of various molecules have been investigated. The molecular layers investigated included donor molecules with relatively high energy HOMO, molecules with high HOMO-LUMO gaps and acceptor molecules with low energy LUMO and terminal alkyl chain. Using an oligo(bisthienylbenzene) based layer, (HOMO energy level in vacuum is close to the Fermi level of the gold bottom electrode) the devices exhibit robust and highly reproducible rectification ratios above 1000 at low voltage (2.7 V). When the molecular layer is based on a molecule with a high HOMO-LUMO gap, i.e. tetrafluorobenzene, no rectification is observed while the direction of rectification is reversed if the molecular layer consists of naphtalene diimides having low LUMO energy level.

We demonstrate that rectification is induced by the asymmetric contact but is also directly affected by orbital energies of the molecular layer. A “molecular signature” on transport through layers with thicknesses above those used when direct tunneling dominates is thus clearly observed.

Quantum transport in magnetostrictive nanocontacts

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Abstract:

One of the main challenges in realising single molecular electronic devices is the control of electronic transport through these devices [1,2]. Fe73Ga27 (Galfenol) is a rare-earth free magnetostrictive alloy which has recently gained a lot of attention due to its large magnetostriction ($\lambda_{001}>3x10^{-4}$) and the ability to retain its magnetostriction value under high mechanical stress. Here, we demonstrate the conductance switching of a melt-spun magnetostrictive Fe73Ga27 (Galfenol) ribbon sample using a mechanically controlled break junction (MCBJ) [3] set up at 10K. Apart from the mechanically controlled conductance switching, we also utilised the magnetostrictive property of Galfenol to control the switching behaviour in such nanocontacts. Fig. 1(a) shows the variation of the conductance as a function of the piezo voltage while closing the contact from an initial open configuration. The observed quantized conductance steps are typical of a few-atom contact and reveal a change in the local atomic arrangement. The histogram in the inset of Fig. 1(a) exhibits a broad maximum at $G/G_0$~0.8 during contact opening and $G/G_0$<1 while contact closing. This may be attributed to the fact that the junction closing occurs much more gradually when the contacts are close together whereas opening of nanocontacts occurs abruptly. Figure 1(b) shows the tunnelling behaviour observed for $G(V)$ and $G(H)$ during closing of the nanocontacts. The linear behaviour of the semi-logarithmic plots for $G/G_0$ vs. piezo voltage and $G/G_0$ vs. magnetic field (Fig. 1(b)-inset) is evidence for electron tunnelling. The electrode distance $\Delta x$ and piezo voltage (or magnetic field) can be related using the equation $G \sim \exp(-\Delta x/\xi V)$, where $\xi V = 0.36$ Å is the average work function of the electrode in helium (7.55 eV).

![Figure 1](image)

Figure 1: (a) Variation of Conductance ($G/G_0$) with piezo voltage while closing the junction for various cycle numbers ($n$). Inset shows the conductance count distribution for opening and closing of the nanocontacts. (b) $G/G_0$ vs. piezo voltage (blue) and $G/G_0$ vs. magnetic field $H$ (red) while closing a nanocontact which shows electron tunneling for $G/G_0$ <<1. Inset shows a straight line fit for the semi-logarithmic plots of the same data indicating a tunnelling behavior in this regime

References:

Quantum Interference in Single-Molecule Anthraquinone Devices

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Abstract:

Anthraquinone (AQ) offers an interesting model system for studying quantum interference (QI) effects in molecular transport. Reversibly reducible from a cross-conjugated form to the linearly-conjugated dihydroxyanthracene (HA), AQ presents an attractive single molecule redox switch 1. Directly correlated to this change in conjugation behaviour is the destructive QI that has been observed in this system 2, resulting in order-of-magnitude differences in conductance between the two redox forms 3. Through the application of an electrostatic gate, AQ-based molecular devices can be charged, lifting the destructive QI in the N state, and allowing for the transport physics to be probed across multiple charge states 4. This system has also been predicted to exhibit Fano resonances, arising from the interaction between localised states on the pendant oxygen groups with the continuum of transport through the conjugated backbone 5. The energetic position of Fano resonances can be tuned through chemical modification of side groups 6, and for AQ this resonance lies around the Fermi level of the electrodes. Due to the proximity of this anti-resonance to the Fermi level, AQ is predicted to display a greatly enhanced Seebeck coefficient making it a promising candidate for thermoelectric applications 7. Recently, theoretical work has shown that the conjugation-based argument breaks down when the connectivity of AQ is changed from para to meta; the destructive QI in the N state is lifted for the meta connectivity and is instead shifted to the N+2 state, electronically equivalent to HA 8. This work aims to verify this hypothesis, and to highlight whether the predicted Fano physics can be observed in this system. Here I will present initial results of charge transport measurements on individual AQ molecules contacted using electroburned graphene nanogaps.

Figure 1: a) ‘para’ and ‘meta’ coupled anthraquinone molecules with tri-alkoxy-pyrene anchor groups. b) Calculated transmission spectra for both para (blue) and meta (red) forms of anthraquinone (AQ) and the related species dihydroxyanthracene (HA) across graphene electrodes (reproduced from 8). c) Example stability and differential conductance diagrams measured for para (top) and meta (bottom) molecular junctions.

References:

Synthesis of new OPE derivatives and a study of their electro-thermal properties in molecular junctions

Herve Dekkiche, Andrea Gemma, Nico Mosso, Thomas Niehaus, Samy Merabia, Bernd Gotsmann and Martin R. Bryce

Abstract:
In the past few years, the development of new devices involving electronic technology have not ceased to increase both in demand and in complexity. With the miniaturization needed to build always smaller computers, smartphones and other tools that came along, new problems arose. Among them, the increase of the heating/power ratio represents one of the biggest issues. The understanding of how electrons, photons and phonons interact together is not very well understood as yet. To tackle that problem, top-down and bottom-up approaches should be exploited. The work presented here is focused on investigating the phenomenon involved at the molecular level. We aim to study the single-molecule electro-thermal conductance of synthetically tailor-made chemical species anchored between the gold electrodes of a custom STM setup. The experimental results obtained will be supplemented with computer simulations which use DFT principles.

Our first targets were based on the oligophenylene-ethynylene (OPE) model. Although being generally less conductive than their vinyl-based homologs, namely the oligophenylene-vinylene (OPV), OPEs offer a good compromise between electron delocalization, chemical stability and synthetical feasibility. A few years ago, oligoynes having a dihydrobenzothiophene (DBT) anchoring group were developed in our group and have proven to be excellent candidates for the study at the gold-gold interface. For that reason, the synthesis of a new series of OPEs having DBT end groups has been investigated. First, the molecules have been prepared with various central units and presented single-molecule conductance values of approximately $4 \times 10^{-4} \ G/G_0$. This result can be corroborated with the electronic density of the first molecular energy levels of the molecules (DFT), which is fully delocalized over the whole molecule. More elaborated species, containing more than one OPE unit have also been studied and their conductance profiles showed very interesting features.

Acknowledgements: We acknowledge funding by the European Commission H2020-FETOPEN project ‘EFINED’, Grant Agreement no. 766853.

References:
Si-Bridged Quinoidal Fused Oligosilole Derivative Single Molecular Transistor with H-ELGP Pt-based Nanogap Electrodes

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Abstract:

Nowadays, many researchers have proposed the next-generation transistors such as fin field-effect transistor (Fin-FET), tunneling field effect transistors (T-FETs), and magnetic field effect transistors (MFETs) toward 3nm technology node, since current logic transistors of Fin-FETs need to overcome the requirements of a reduction in leakage current. Here, we demonstrate molecular transistors based on Si-bridged quinoidal fused oligosilole derivative (Si-2). Quinoidal fused oligosilole derivative (Si-2) used in this study is a strong candidate of functional group for molecular devices due to good structural stability for change in the valence charge. Si-2 molecule which has a 20π-conjugated molecular structure with two silicon atoms in Figure 1 was introduced between hemispheric electroless Au-plated (H-ELGP) Pt-based nanogap electrodes owing to two ethanethiol groups with strong S-Au chemical bond. Figure 2 shows $I_d-V_d$ and $dI_d/dV_d-V_d$ characteristics with gate voltage dependence at 9K. Gate voltage dependence on $I_d-V_d$ characteristics are clearly observed, and on/off ratio ($I_{on}/I_{off}$) is as high as 80 under $V_d$ of 200 mV.

This study was partially supported by MEXT Elements Strategy Initiative to Form Core Research Center from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan; and the BK Plus program, Basic Science Research (NRF-2014R1A6A1030419).

References:
Molecular junctions based on ruthenium complexes

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The research efforts devoted to the design and the incorporation of ruthenium complexes onto ordered arrays systems are driven by their potential use as building blocks in molecular electronics, especially in the elaboration of photoactive surfaces. The long-lived excited state lifetimes of the 3MLCT excited state is especially of interest for a multitude application such in, e.g., heterogeneous catalysis, chemical and biological sensors, electrical and optical thin-film devices, and optics. Electrodeposition of aryl diazonium salts has been used as an alternative efficient method to functionalize surfaces with a strong covalent bond between the reagent and the electrode. Bulky substituted bi or ter-pyridine ligands have been designed to generate ruthenium complex monolayers. Robust molecular junctions using naphthalene diimine substituted terpyridine ligand and unexpected self-organized monolayer using novel fluorene substituted bipyridine ligand will be presented and fully characterized by AFM, XPS, electrochemistry and STM. Bipolar light emission and charge transport in symmetric molecular junctions based on [Ru(bpy)₃]²⁺ or [Ru(bpy)₂ppy]⁺ oligomers will be also presented.

(4) Q. V. Nguyen, F. Lafolet, P. Martin, J.-C. Lacroix, submitted
Molecular Wires without Bond Length Alternation

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Abstract:
Molecular conductance normally decreases exponentially with increasing the length of a molecule. However, molecules with small bond-length-alternation (BLA) are predicted to have lower HOMO-LUMO gaps, which may compensate for molecular elongation. 1,2 We chose cyanine dyes and their rotaxane derivatives as our research topic. These are molecules bearing π-conjugated polymethine bridges without BLA and presenting lower HOMO-LUMO gap as their carbon chain length increases. 3,4 Using α-cyclodextrin to protect the cyanine dyes not only improves their stability,5 but also prevents the molecules from aggregation, which may facilitate molecular conductance measurements. We are interested in exploring the relationship between molecular length, conductance and attenuation factor (β) within this family of dyes, and we are exploring the distance-dependent conducting properties and the ability to mediating long-range charge transport of the cyanine dye molecules. (Related work from another group was reported recently. 6)

References:
Single charge electronics with gold nanoparticles, organic monolayers and semiconductor substrates

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Highly controlled organic layers offer flexible and tunable materials to control the electronic properties of ultrathin materials. For example such layers can be used for connecting nanosize electrodes such as metallic nanoparticles. Particles serve as the core element of assemblies where the electrical current is reduced to the smallest possible since electrons are controlled one by one by using the Coulomb blockade phenomenon. Here we describe how we combined ordered monolayers on silicon with nanoparticles to study fundamental properties of charge transport at the nanoscale.

We prepared colloidal gold nanoparticles of 6 nm and grafted them on a grafted organic monolayer (GOM) on silicon. GOM are highly ordered monolayers prepared by hydrosilylation of alkene molecules and subsequently modified with an amine group so that gold nanoparticles can be firmly immobilized on top of the layer. A wide range of characterization methods were used to assess the preparation: AFM, STM, Scanning Tunnel Spectroscopy (STS), High Resolution-TEM, XPS, FTIR and UV-visible spectroscopy [1, 2].

We will discuss several electrical properties at a single electron level. By placing an STM tip above a nanoparticle, Coulomb blockade allows controlling the number of electrons simultaneously injected in the nanoparticle [1, 3]. Using the conductive tip of KPFM, we were also able to reveal the spontaneous charging behavior of the gold nanoparticles [3]. This opens the way for new kinds of single electron memories or single electron transistors.


New architectural molecular junction

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Abstract:

A classical way to study molecular junctions is to work with a top and down electrode. The problem of this architecture is to have a large surface and no control over the characterizations with and without molecular. This work presents new architectural molecular junctions where we can study before and after molecule grafting and an easy accessibility to the molecule.

Molecular junctions were fabricated with the combined use of electrochemistry and conventional CMOS tools. They consist of a 15 nm thick layer of anthraquinone between two gold electrodes. The layer was grafted between the two electrodes using diazonium electroreduction, which yields a stable and robust gold–oligomer interface. The contact was obtained by the growth of the anthraquinone film between the two electrodes. Transport mechanisms across the layers were investigated by analysis of current–voltage (I–V) curves.

References:

Quantum interference induced enhanced thermoelectricity in molecular junctions

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Abstract:
Nanoscale junctions embedding designed molecules and taking advantages of quantum interferences are predicted to enhanced thermoelectricity. This would lead to a better recovery of heat-wasted energy and increase the energetic efficiency of many devices.

My Ph.D. just started in April and is focused on the growth of graphene by chemical vapor deposition and reactive ion etching. The next step is the fabrication of nanodevices on silicon chips using E-beam lithography and metallic evaporation. Electrical breakdown in a probe station is then performed on the graphene junctions to make nanogaps. The desired molecules, graphene nanoribbons (GNRs) or gold nanoparticles are then deposited in the junctions where they electrically connect the two graphene electrodes. Electronic measurements are performed before and after the deposition to observe the differences and measure thermoelectric properties.

In this poster, I will present the fabrication of the graphene and gold nanoparticles, the devices on the silicon chip. I will explain the electrical breakdown as well as the deposition of the molecules, GNRs and gold nanoparticles in the junctions. Finally, the already obtained results and the future objectives will be presented.
Electrical wiring of dehydrogenases at flexible and redox-active carbon nanotube buckypaper electrodes towards body-integrated energy-harvesting

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Abstract:
Buckypapers is a randomly oriented self-supporting film of carbon nanotubes, resembling an electronic paper, with excellent prospects for a plethora of applications ranging from aerospace materials to sensors, actuators and fuel cells. Over the last 5-7 years, buckypaper materials have emerged for the construction of bioelectronics devices, including implantable and wearable biofuel cells, owing to properties including high electrical conductivity and porosity, light weight and flexibility, and the possibility to electrically connect enzymes and microbes. This talk will describe the development of lab-made and commercial buckypaper electrodes and their functionalization with different organic and inorganic electro-active redox molecules, and polynorbornene polymers, for the electrical wiring of glucose dehydrogenases. Most enzymes do not exchange electrons with electrodes on which they are adsorbed but this talk will reveal several types of functionalized electrode which promote electron and substrate transfer for electro-enzymatic glucose oxidation. The ultimate goal of this work is to obtain compact, flexible and catalytically powerful electrodes for a new generation of body-integrated biofuel cells.

References:


Magnetic field control of the Franck-Condon electron-vibron coupling in a carbon nanotube

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Abstract:
Suspended carbon nanotubes display at cryogenic temperatures a distinct interaction between the quantized longitudinal vibration of the macromolecule and its embedded quantum dot. It becomes visible via Franck-Condon side bands in the single electron tunneling current, with clear quantized harmonic oscillator behaviour [1,2].

Here, we present first data on such Franck-Condon side bands in a clean, as-grown suspended carbon nanotube device [3], at known absolute number \( N = 1 \) and \( N = 2 \) of conduction band electrons and consequently well-defined electronic ground and excited states. The electronic system is localized at the center of the nanotube, far away from any metal contacts; the electronic transport spectrum indicates unperturbed one- and two-electron states.

The Franck-Condon side bands evolve only at a large magnetic field parallel to the carbon nanotube axis, and display a distinct magnetic field dependence of the Franck-Condon coupling parameter \( g \). The coupling is different for different electronic base states, indicating a valley-dependent effect [4]. Tentative models are discussed.

Differential conductance as function of magnetic field and bias voltage, displaying the evolution of harmonic side bands at the edge of the 2-electron ground state single electron tunneling region.

Inset: Trace cut, with the side bands highlighted.

References:
Transport properties of tungsten disulfide nanotubes

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Abstract:
Research on carbon nanotubes has led to a multitude of insights regarding low temperature transport spectroscopy. However, while synthesis procedures for tubular morphologies of layered materials other than graphene are well-known [1, 2, 3], their transport properties are largely unexplored [4]. Here, we introduce transition metal dichalcogenide (TMDC) nanotubes as a new material platform for transport spectroscopy. We present results on optimized nanotube synthesis, first device fabrication, and electrical characterization.

WS2 and MoS2 nanotubes are synthesized using a chemical transport reaction. Optimized growth parameters lead to thin nanotubes with diameters down to 10nm, lengths up to several millimeters, and an extremely low number of structural defects. Transferring tubes from the growth substrate yields individual macromolecules which are then localized and contacted using electron beam lithography. We observe both p-type and ambipolar behaviour, depending on the contact metal.

References:
Printed electrolyte gated field-effect transistors from graphene oxide formulations: electrochemical tuning of charge transport

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Graphene-based materials have lately become a subject of many researches due to their extraordinary properties such as high intrinsic mobility, good electrical conductivity, and a wide range of potential applications such as biosensors. In particular, graphene-based field-effect transistors (GFETs) offer interesting perspectives due to their high sensitivity. By applying the appropriate potential to the gate, it is possible to modulate the charge carriers’ concentration in the graphene-based channel of the GFET. Among the different fabrication techniques, inkjet-printing is particularly interesting as it permits fabricating this kind of devices outside the clean room, thus saving time and reducing costs.

In this work, the goal is to combine these two approaches. A home-made graphene oxide (GO) formulation is used as active material for the channel and is deposited by inkjet-printing. Among many ways to reduce GO, we developed an in situ electrochemical approach to obtain conductive reduced GO (rGO) directly on the device. The morphology (Fig. 1a) of the printed rGO layer as well as its electrical properties in electrolyte-gated configuration (Fig. 1b) are investigated. Our transfer curves show a strongly marked Dirac point (Fig. 1c) and ambipolar behavior as previously described.

Surprisingly, transfer curves exhibit a drastic evolution with the reduction degree of GO, which we will discuss. Our results pave the way to the electrochemical control of charge carrier transport in rGO-based materials.


Figure 1. (a) AFM image of inkjet-printed GO layer on interdigitated electrodes on silica substrate, (b) GFET setup in electrolyte gated configuration, (c) transfer curves of GO and rGO at different reduction times.
Electrochemical gating for single-molecule electronics with graphene contacts

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Abstract:
The single-molecular conductance of a redox active viologen molecular wire bridged between Au/graphene electrode has been studied in an electrochemical gating configuration in the 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIOTf) ionic liquid environment. The scanning tunneling microscopy (STM) based $I(s)$ (where $I$=current, $s$=distance) non-contact method has been used to measure the conductance value as a function of the electrode potential, as shown in Figure a. An effective electrochemical gating of molecular junction has been achieved using an electrochemical STM with biopotentiostat control. Observed plateaus containing $I(s)$ traces indicated the successful forming of molecular junctions as shown in the inset of Figure b. Here, A clear “off-on-off” conductance switching behavior was obtained through gating of the redox state when the electrode potential is swept from positive to negative potentials. Au/viologen/graphene junctions showed a single-molecule conductance maximum centered close to the equilibrium redox potential as shown in Figure b. We found that the conductance of Au/viologen/graphene junctions is significantly higher than the standard Au/viologen/Au junctions. Compared to Au/Au contacts, a more obvious gating effect was also observed for asymmetric Au/viologen/graphene junctions. Density Functional Theory (DFT) and electronic transport calculations support the measured data. These results highlight the important role of the contact material for molecular devices and show the potential application of graphene electrode material.

Figure:

a) Schematic diagram of the electrochemical STM-based $I(s)$ technique, the inset shows the four electrodes systems with two working electrodes (STM tip and graphene substrate), Pt counter electrode and Pt reference electrode. The counter and reference electrode provide the gate electrode in this four-electrode biopotentiostat setup with independent electrochemical potential control. b) The conductance values measured for Au/6V6/graphene junctions in BMIIM-OTf electrolyte are plotted as a function of substrate electrochemical potential. Inset: The plateau contained $I(s)$ traces of Au/6V6/graphene.

References:
Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature

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The quantum interaction between molecules and electrode's material at molecules/electrode interfaces is a major ingredient in the electronic transport properties of organic junctions. Driven by the coupling strength between the two materials, it results mainly in a broadening and an energy shift of the interacting molecular orbitals. Using new electrodes materials, such as the recent semi-conducting two-dimensional nanomaterials, has become a recent challenge in the field of molecular/organic electronics that opens new possibilities for controlling the interfacial electronic properties and thus the charge injection properties.

It has been shown that to introduce asymmetry (rectification) in the electronic response of molecular and organic junctions, it is necessary to introduce an asymmetry along the transport direction²,³. This can be achieved either by using different contact electrodes (i.e. with different injection properties), and/or by using asymmetric anchoring moieties or molecular structures as originally proposed by Aviram and Ratner⁴. Recently, we have shown that based on diazonium approach oligo-BTB form high quality organic layer and lead to highly stable organic junctions.⁵-⁷ Those organic diodes presented large rectification ratio RR of 1000 and we clearly demonstrated that the rectification behaviour in this configuration is an evidence of molecular signature even if the two metallic electrodes have different Fermi energies. Several molecules have been tested into junctions and the RR varied from 10⁻² to 10³ with a very good reproducibility and same conditions.⁸

We report the use of atomically thin two-dimensional multilayer graphene films as base electrode in organic junctions with a vertical architecture. The interfacial electronic structure dominated by the covalent bonding between bis-thienyl benzene diazonium-based molecules and the multilayer graphene electrode were probed by ultraviolet photoelectron spectroscopy and the results compared with those obtained on junctions with standard Au electrodes. Room temperature injection properties of such interfaces were also explored by electronic transport measurements. We find that, despite strong variations of the density of states, the Fermi energy and the injection barriers, both organic junctions with Au base electrodes and multilayer graphene base electrodes show similar electronic responses. We explain this observation by the strong orbital coupling occurring at the bottom electrode/ bis-thienyl benzene molecules interface and by the pinning of the hybridized molecular orbitals.

Adsorbate Induced Changes on the Metallicity of the Quasi-One-Dimensional Electron System of the Si(553)-Au Surface, Studied by Infrared Spectroscopy

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Abstract:
Plasmonic signals of quasi-one-dimensional electron systems, for example, related to atomic gold wires on vicinal Si(553), are a direct measure of their metallic properties. Because of the finite length of the ordered atom chains on real surfaces, a localized plasmonic excitation can be measured with infrared (IR) spectroscopy. The measured IR signals are extremely sensitive to changes of the metallic behavior, for example, due to the exposure to hydrogen [1] or the deposition of additional gold atoms [2]. We also observed strong spectral changes for oxygen exposure which can be ascribed to a transition towards an insulating state, similar to the behavior under hydrogen exposure and with gold adatoms, respectively. For C70 [3] and TAPP-Br (a core brominated TAPP derivate [4]) deposition, the plasmonic signal almost keeps its original strength up to the coverage of many monolayers. But, differently to C70, TAPP-Br exposure results in a huge shift of the resonance position to higher frequencies and a strong increase of the electronic damping, indicating a stronger confinement of the free charge carriers in the quasi-one-dimensional channel due to the adsorbate coverage [5].

References:
Enzymes for electronics in analytical devices

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Abstract:
The current demands of sustainable green methodologies have increased the use of enzymatic technology in industrial processes. Employment of enzymes as biocatalysts offers the benefits of direct electron transfer (DET). DET-type bioelectrocatalysis of redox enzymes is an essential technique for constructing bioelectrochemical devices such as biosensors, bioreactors, and biofuel cells. Significant breakthrough has been achieved by using various conductive nanoparticles to promote the direct bioelectrocatalysis. Enzymes can be attached to nanoparticles in a "wired" configuration, i.e. one that provides a conducting path to facilitate mediatorless electron transfer between the protein redox center and the electrode or between the redox centers of two different proteins [1–6]. For this reason we synthesized a few types of graphite or magnetic nanoparticles using different protocols and tested as the matrix for the bioelectrocatalytic systems working with glucose dehydrogenases from Acinetobacter calcoaceticus, Ewingella americana, urease from Canavalia ensiformis and laccase from Didymocrea sp. In the presence of the analyte – respective substrates of the enzymes – the electric current (response) is generated. Based on these approaches the urea analyzer for fertilizer analysis has been developed and the practical application of device has been demonstrated.

References:
Formation of nano-carbon sheets from two dimensional self-organized structures of organic molecules via on surface reaction

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Abstract:

Graphene composed of carbon atoms arranged in a two-dimensional hexagonal lattice is a promising for device application. With the progress of research in recent years, various fascinating properties has been confirmed, while the proto-typing of various electronic devices using graphene has been also tried. However, fundamental growth technique of graphene sheets is still under development. In many cases, the most widely used technique is a metal-catalysed CVD. By means of this method, it is possible to prepare large area graphene sheets at a practical growth rate, however, its quality must be much more improved towards device applications. Another promising technique is a thermal decomposition of SiC under ultra-high vacuum condition. In this method, all processes are carried out in a clean vacuum environment, so that graphene sheets with few defects and impurities can be obtained. On the other hand, since the materials is exposed to an extremely high temperature more than 1300°C, integration with other device components and processes are difficult. As a method combining the advantages of these two methods, we developed a local CVD reaction system under high vacuum condition. By means of this method, high-quality graphene sheets can be produced at a relatively low reaction temperature of about T=800°C in a clean vacuum environment. However, the growth speed of sheets is extremely slow, and improvement in order to obtain large area graphene sheets is still demanded. In this reaction, it has been found that, prior to the formation of graphene sheets, lamella-like structures in which molecular chains are densely packed and conjugated, are formed as preliminary structure of graphene. Since the formation and conformation of lamellar-like structures observed is similar to the self-organized structures of organic molecules on the surface, it seems reasonable that sheet formation process is improved by replicating these preliminary structures by self-organized structures of organic molecules. Figure 1 shows a molecular resolution STM image of triacontane molecules (C_{30}H_{62}) self-organized on Cu (111) surface under UHV condition. When this structure was gradually heated in a vacuum, uniformed self-organized structures deformed to small patches of several nano-meters around T=400°C and finally the image of molecules became structure-less around T=800°C as shown in Figure 2. By means of XPS obtained from the surface using synchrotron radiation indicates that both sp^2 hybrid orbital and sp^3 hybrid one of carbon atoms were simultaneously existed. This result suggests that reactions towards formation of graphene sheet are progressing on the substrate from self-organized structure by triacontane via on-surface reaction.

Figure 1 shows a molecular resolution STM image of triacontane self-organized on Cu (111) surface. Figure 2 shows a STM image of surfaces shown as figure 1 after heat treated in UHV.

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Selective growth of Metallo-Tetraphenylporphyrin Nanowires by Post-Growth Processes

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Abstract:

Controlling self-organization of small organic molecules in nanostructures with the desired shape and size is one of the main challenges in organic nanoelectronics. Here, a strategy for selectively growing uniaxially aligned nanowires of meso-tetraphenyl porphyrin-Zn(II) (ZnTPP, Fig. 1a) is presented, based on post-growth processes. ZnTPP is deposited by Organic Molecular Beam Epitaxy on potassium hydrogen phthalate (KAP), an organic salt easily giving cm-sized single crystals, demonstrated to be particularly suitable as substrate for organic epitaxy. The as-grown films typically display a rather rich surface morphology, characterized by the presence of nanowires and other nm-sized aggregates (see Fig. 1b). Properly tuned aging processes in vacuum and in air are demonstrated to be a tool for the selection of crystalline ZnTPP nanowires, with controlled crystal structure, shape and size, and with uniaxial orientation (see Fig. 1c), at the expenses of the other phases via quasi-Ostwald ripening. This phenomenon is driven by organic epitaxy between the matching crystal surfaces of ZnTPP and KAP. The ability of growing ZnTPP nanowires with a unique crystal structure and precise orientation gives the chance to study the intrinsic properties of the triclinic polymorph of ZnTPP, such as the role of intermolecular interactions in driving its optical response.

Figure 1

a) Molecular structure of ZnTPP: H atoms in white, C atoms in grey, N atoms in light purple, Zn atom in blue; AFM height (5 x 5) µm² images of a ZnTPP sample grown on KAP, one (b) collected immediately after growth and the other one (c) collected after applying a proper post-growth aging protocol, aimed at selecting the nanowires. The color scale and the orientation of the [001] KAP axis on the right apply to both panels.
Quantifying the Impact of Covalent Functionalization on Surfaces using Diazonium Chemistry

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Abstract:

Covalent modification of surfaces is targeted to explore the fundamentals underpinning the manipulation of material properties. Model graphite surfaces as well as applied graphene materials have been characterized. Initially, surfaces are covalently modified using electrochemically activated aryl diazonium chemistry. [1] We subsequently established quantitative links using scanning tunneling microscopy (STM), Raman spectroscopy, and photoelectron spectroscopies (Fig. 1). The degree of chemisorption on the graphite surface is altered by varying the diazonium concentration and the electrochemical activation parameters. Experimental connections between inter-defect distance and spectroscopic signatures provide a new understanding of the microstructural impacts that result from covalent modification. Angle-resolved photoemission spectroscopy reveals the effects of covalent modification on the electronic band structure of graphene materials. Overall, this work establishes fundamental knowledge on the manipulation of surface matter with molecular level insight.

Figure 1: STM visualizes varying densities of covalent aryl-functionalization of graphite surfaces. Inset represents the corresponding Raman spectrum indicating the degree of chemisorption by the rise of the D-peak around 1334 cm⁻¹.

References:

Self-Assembly 3D Electronic Structures on the 2D Supramolecular Tectons

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Abstract:

Self-assembly of supramolecular 2D building blocks (tectons) has emerged as an important process to pattern well-organized monolayers on 2D materials. One of the 2D materials, Graphene has good physical properties, especially electronic, optical, and mechanical properties, but bandgap tuning is required for semiconductor properties for a wider range of applications. As one of the tuning methods, it is possible to synthesize materials with unique characteristics by using a self-assembly. Electrically active molecules are synthesized through a molecular DFT calculation and design. The molecules were self-assembled in nanohole of the graphene with tecton array by drop-casting method. The self-assembly structures confirmed by scanning tunneling microscopy at the air/solid interface on the large-scale. This self-assembly 3D electronic structures can be applied for new electronic devices such as nano-thermoelectric harvesters, optoelectronics, and transistors.

References:

Tuning the optical and self-assembly properties of small diketopyrrolopyrrole derivatives through multiple hydrogen bonding

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Abstract:

π-Conjugated systems, polymers and small molecules, are extensively employed in the field of organic electronics. 1 Both, the optoelectronic properties and the structural aspects of these systems have to be optimized to reach good performance in the final applications. Supramolecular chemistry is an alternative to achieve such control, especially when using small molecules. This way, it is possible to build semiconducting systems where the electroactive motifs are precisely organized by noncovalent interactions into functional supramolecular polymers.2 The incorporation of highly directional noncovalent interactions, such as hydrogen bonds (H-bonds) can guide the self-assembly processes and vary the electronic properties. H-bonds are sensitive to solvent, concentration and temperature. Furthermore, the number, position and strength can deeply impact the self-assembly processes, influencing the final properties. H-bonds have been used in several types of organic electronic devices, such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and solar cells. In these examples, the H-bonds afforded better connection among semiconductors, and thus very appropriate structures for charge transport.3 Here we show that just by functionalizing simple thiophene-capped diketopyrrolopyrrole (DPP) derivatives with semicarbazone4 or amide units, the optical and self-assembly properties can be tuned while controlling the formation of H-bonding. The appearance of J-type aggregates reaching the NIR region upon H-bonding formation made possible to vary the energy band gap and supramolecular structures formed in solution and on thin films. A combination of variable temperature UV-Vis spectroscopy, Fourier transform infrared (FTIR), circular dichroism (CD) and microscopy has been used to unravel the assemblies formation and the impact on the electronic properties.

References:

Nonvolatile Memory Effect in Self-Assembled Monolayers Based Molecular Junctions

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Low-cost and chemically tunable organic materials are promising to construct memory devices¹-². Self-assembled monolayers (SAMs)³ or single molecule⁴,⁵ based memory devices have attracted considerable attention as they can provide new switching mechanisms. In general, it is still challenging to obtain reversible switching with large on/off ratios driven by electric field in molecular junctions. Here we report a voltage driven nonvolatile memory effect in viologen SAM based molecular junctions with an ON/OFF ratio of >10³. In addition, we also found that the memory effect is counterion dependent with I⁻ gives the largest ON/OFF ratios, but ClO₄⁻ results in junctions without a memory effect. Cyclic voltammetry was performed for the viologen SAMs and showed the dimer formation of the radical cation of the reduced viologen⁶ which may be responsible for the conductance switching. In conclusion, this work can provide new insights for nonvolatile voltage-driven SAM-based memory.

Polyoxometalate-functionalized vertically-oriented silica thin films for molecular electronics applications

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Abstract:

Metal-molecule junctions are the key components of molecular electronics circuits. Fundamental differences have been encountered between single-molecule and ensemble junctions. The main conceptual difference between idealized molecular and ensemble junctions is that in the latter case the interaction of individual molecules becomes important and determines the scaling of charge transport properties which depend on the number of molecules the junction contains. While in some experimental studies the conductance per molecule has been observed to scale directly with the number of molecules in the junction, in other cases the current per molecule in single molecule junctions has been found to be several orders of magnitude larger than for the monolayer.

Polyoxometalates (POMs) are inorganic building blocks analogous to molecular oxides.1 They can accept and delocalize supplementary electrons within their molecular framework without undergoing structural damage.2 We are currently investigating if an approach to address these issues would be the measurement of the conductance of molecular wires confined in vertically-oriented mesoporous silica films with pore diameters of 2-3 nm.3 In this case, silica will play the role of a template allowing the isolation of molecular clusters immobilized inside the pores with a regular and convenient configuration for the measurement of the charge transport through the device. The proper choice of the molecular components and the host geometrical constraints produces a precise control of the supramolecular organization of the inserted molecules, thus tailoring the properties of the resulting system by preventing aggregation even at high concentration.

The convenient processability of silica sol-gels compounds, especially organic-inorganic hybrids, lead to interesting materials for optics, molecular electronics, catalysis or electro-catalysis.4,5 The use of the vertically-oriented silica-based films will provide the possibility of creating an organized network which will be employed to confine POMs by using several strategies. Up to three different approaches to functionalize vertically-oriented silica thin films with polyoxometalates (POMs) will be presented. They are based either on the formation of covalent bonds or on the electrostatic interactions between the anionic polynuclear metal oxo-clusters. A full characterization of the POM-functionalized silica thin films will be presented in order to establish the best strategy to immobilize these species inside ordered and oriented silica matrices with potential applications in electronic devices due to their electron reservoir behavior.

References:

Reversible photoisomerization inside a 2D self-assembled layer of diarylethene molecules

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Abstract:

This study comes within the framework of design and study of smart surfaces. They are based on the self-assembly of functionalized molecules on a substrate, that will respond in a defined way to an external stimulus. As the use of light to control smart surfaces seems to hold promising prospects [1, 2], diarylenes [3] are one of the most appropriate functionalized molecules for the achievement and study of smart surfaces. They are photochromic, i.e. they undergo a reversible phototransformation at specific wavelengths between two stable conformations with markedly different optical and electronic properties.

In this study, we report an in situ reversible photoisomerization inside a self-assembled layer of diarylethene molecules on a graphite surface at the solid-liquid interface. To achieve this aim, a new diarylperfluorocyclopentene derivative has been designed and synthesized, bearing benzothiophene groups in order to improve its fatigue resistance compared to diarylenes with thiophenes [3]. Its photochromic properties have been investigated by a UV-visible study in solution. A submolecularly resolved scanning tunneling microscopy study shows that both open and closed isomers form a self-assembled layer on HOPG at the solid-liquid interface, with markedly different organizations. UV and visible light irradiations lead to reversible isomerizations of the molecules inside the 2D self-assembled layer. It is also possible to improve the self-assembly of the closed molecules by using light irradiation cycle. As photoswitching is proved to happen in the supramolecular self-assembly and not in solution through a desorption-readsorption process, these results may pave the way to get photoresponsive smart surfaces based on diarylenes solely.

STM pictures and corresponding schemes presenting the self-assembly of antiparallel-open (on the left) and of closed (on the right) diaryl-(TBT), molecules on HOPG at the solid-liquid interface.

References:

Hybrid self-assembly of quantum dots and gold nanoparticles driven by protein pairing

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Abstract:

The broad field of nanotechnology has resulted in the design of hybrid nanomaterials featuring exclusive properties such as sensing, data or energy storage and biocide activity. Molecule-driven self-assembly of biomolecules led to the design of colloidal assemblies thanks to the direct recognition of specific molecular partners grafted onto nanoparticles. Direct coupling of nanoparticles has been achieved using DNA strands hybridization, peptide coupling or archetypal protein interactions (streptavidin and biotin) but these methods are either expensive or either restricted to the limits of their assembly mediators. Recently, novel massive assemblies of gold nanoparticles were designed using artificial repeat protein pairs (αRep protein pairs).\textsuperscript{1} These new and promising assembly agents are able to organize functional colloids and provide control on the interparticle distance. Moreover, αRep proteins exhibit hypervariable amino acids positions that provide tremendous possibilities of interacting partners such as another protein or a specific crystalline surface.\textsuperscript{2}

In this contribution, we present the design of new homogeneous and hybrid αRep proteins driven self-assemblies of semiconductor nanoparticles (Quantum dots, QDs) and gold nanoparticles (nPAu).

First, the functionalization strategies of QDs and nPAu consists in using a polycystein peptide before grafting on both αRep proteins onto these nanoparticles. The grafting on both αRep proteins onto these nanoparticles is characterized using agarose gel electrophoresis showing the saturation of their surface. The affinity of protein-functionalized nanoparticles is then characterized using surface plasmon resonance technique. Mixtures of complementary nanoparticles populations are observed under transmission electronic microscopy and show the formation of large colloidal assemblies (Figure 1). The optical properties of these aggregates are finally characterized by fluorescence spectroscopy. These results give hope to design other hybrid colloidal assemblies in order to be used as new optical nanostructures.

Figure 1: Schematic representation of the three steps process of production of hybrid self-assemblies (left) and TEM image of self-assembled QDs and nPAu (right).

References:


Nanoconfinement of $[\text{Fe(bpy)}_3]^{2+}$ in ordered vertically aligned silica thin films

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Abstract:

The phenomenon of spin crossover (SCO) for the Fe$^{II}$ consist to the change of molecular spin state by the effect of either photoexcitation, temperature or pressure. $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$ is an SCO complex which can switch from low-spin (LS) to high-spin (HS) state only by photoexcitation.

We present here a novel methodology employed to confine this mononuclear complex, $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$, in the matrix of a sulfonate-functionalized vertically-aligned mesoporous silica thin film electrodeposited on indium-tin oxide electrode by an electrochemically-assisted self-assembly (EASA) method. Transmission electronic microscopy (TEM) reveals that the mesostructure and orientation of the sulfonate-functionalized silica films is maintained up to 30% of mercaptopropylsilane in the starting sol.

The electrochemical characterization of the $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$ confined in the mesoporous silica shows a stable and reversible signal around 0.86 V. Comparison of the Raman spectrum of the $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$ functionalized silica thin films with the $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$ microcrystalline powder presents the same vibrational bands except in the low wavenumber region corresponding to Fe-N stretching vibrations modes suggesting a change of the conformation of the complex upon its confinement in the silica matrix. The UV-Visible spectrum shows the metal-to-ligand charge-transfer (MLCT) transition of $[\text{Fe}^{II}(\text{bpy})_3]^{2+}$ in silica at 526 nm which is slightly shifted compared to the bulk observed at 519 nm indicating a possible drop of energy gap between LS and HS due to the confinement. This could be then exploited to induce unprecedented thermally induced SCO by modifying the bipyridine (bpy) ligand with methyl group. Such compounds could be interesting for opto-magnetic or opto-electronic sensors.

References:


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The utility of molecular actuators in nanoelectronics requires responsiveness to electric charge by mechanical motion at the interface with conductive surfaces. We hence functionalized redox-active resorcin[4]arene cavitands with thioether groups and investigated their propensity to act as electroswitchable actuators that can adopt two conformations in response to changes in external potential. Molecular design was probed by Density Functional Theory (DFT) calculations that suggest covalent binding of the cavitands to the Au surface in a preferentially upward orientation. The electronic properties were experimentally studied by cyclic voltammetry on Au electrodes, while redox interconversion between the oxidized (quinone, Q) and reduced (semiquinone radical anion, SQ) state was monitored by UV-Vis spectrotelectrochemistry and EPR spectroscopy. It was shown that the reduction to the SQ dianions induces a conformational change to a closed form, providing the basis for voltage-controlled molecular actuating devices in the future.

Figure 1. Top: Schematic representation of a binary switch between an open (kite) form in the oxidized Q state, and the closed (vase) conformation in the reduced SQ radical dianion state of quinone-based cavitands. NQ: naphthoquinone , TQ: triptycene-quinone Bottom: Structure of thioether-functionalized resorcin[4]arene cavitands 1–2 employed in this study.

Carbohydrates electrografting for antifouling applications

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Abstract:

Marine fouling is a phenomenon that takes place when a surface is immersed in seawater. Thousands of marine organisms as bacteria, barnacles, algae settle on the surface causing environmental, economic and material issues. [1] Numerous solutions as self polishing paints based on tributyl tin (TBT) used as a biocide have been developed but are today banned for environmental reasons. E. M. Scanlan et al. have shown that carbohydrates grafted by reduction of salt diazonium on glassy carbon surface were able to limit the adhesion of proteins on surface. [2] Our research group has also demonstrated that electrical solicitations of terthiophene bound to polya crylates could prevent bacteria from settlement on the surface by oxidation of conjugated system at low potential. [3]

Our project is about the immobilization of carbohydrates linked to electroactive systems on glassy carbon or PPF surfaces to target antifouling properties at different levels. Carbohydrate should have an effect on proteins whereas electroactive systems under electrical solicitations should prevent microorganisms from settlement on the surface. So, with reference to our study, we have synthesized 4-aminophenyl-β-D-glucopyranoside (Figure) and ferrocene derivative that have been electrochemically immobilized on glassy carbon and PPF surfaces by amine oxidation. The unprotected glucoside layers were analyzed by XPS, AFM, CV and contact angle experiments. Results demonstrate that the carbohydrate-functionalized surfaces retain the desirable properties of the glucoside compound, producing a wetting-enhancing effect and permitting the electrochemically controlled release of a glucosyl cation equivalent by oxidative cleavage of the anomeric glycosyl–O bond. [4]

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Fluorescence switching via supramolecular plasmonic assemblies

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Tuning fluorescence reversibly and at nano-scale is of great interest for applications in sensing and photo-electronic devices. It is known that both fluorescence quenching and enhancement depend supra-linearly on the distance between the fluorophore and the plasmonic nanostructure. We thus propose to combine supramolecular self-assembly with plasmonics to design a dynamic system allowing reversible tuning of the nanoparticle/fluorophore distance and thereby the resulting fluorescence. We recently succeeded in the fabrication of gold nanoparticles (Au NPs) coated by thermoresponsive polymer poly(N-isopropylacrylamide) (pNIPAM) containing fluorescein (FAM) at the solution-facing end (Fig. 1). The size of the obtained nano-assemblies was characterized by AFM and DLS, while their optical properties were studied by UV-visible and fluorescence spectroscopies. The heat-induced shrinking of pNIPAM resulted in shortening Au NP/FAM distance, causing stronger fluorescence quenching, which was reversible upon cooling to room temperature (Fig. 1). Our current work is focused on the optimization of fluorescence modulation and extending the concept to other stimuli and plasmonic surfaces.

Figure 1. T-driven nano-assembly (left) and the resulting fluorescence modulation (right).
Exploring a Combination of Halogen and Hydrogen Bonds in Two-Dimensional Self-Assembly at the Solution-Solid Interface

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Abstract:

While hydrogen bonding is arguably the most predominantly encountered noncovalent interaction in molecular self-assembly processes, another type of intermolecular interaction called halogen bonding is rapidly evolving as a routine and predictable tool in supramolecular chemistry. Halogen bonds are formed between halogen atoms present on one molecule (typically Br, Cl, or I) and a nucleophilic atom/moiety present on the same or other molecule. Halogen bonds are weaker than typical hydrogen bonds but are highly directional, even more so than hydrogen bonds. These interactions have recently been used in the design of complex and functional supramolecular systems\textsuperscript{[1]}.

In the present research work, a combination of halogen and hydrogen bonds have been employed to fabricate complex two-component supramolecular architectures on a solid surface. Isonicotinamide has been used as a building block which has a hydrogen bonding unit in the form of the amide functional group and a halogen bond acceptor in the form of a pyridinic nitrogen. These unique structural features allow it to co-assemble with halogen bond donors such as 1 or 2 resulting in a two-component co-assembled system stabilized by halogen as well as hydrogen bonds (see Figure 1 below). The self-assembled monolayers so formed have been characterized using state-of-the-art scanning tunneling microscopy (STM) which reveals the contribution of the various above mentioned interactions in the self-assembly process.

Figure 1. Molecular structures of nicotinamide and the halogen bond-donating building blocks 1 and 2. As depicted in the assembly schematic, halogen bonds (X-bonds) will be formed between the pyridinic nitrogen of nicotinamide and the iodine atoms

References:
Synthesis and characterization of SAM’s containing C60-Bodipy dyads bearing helical peptides for organic electronic applications.

Jad Rabah, Van Bui, Hélène Fensterbank, Rachel Méallet-Renault, Karen Wright, Anne Vallée, Emmanuel Allard.

Abstract:

Photoinduced electron transfer (PET) in molecular systems plays a crucial role in converting solar energy to electricity through the use of photovoltaics or storing light energy in the form of chemical bonds. In this perspective, it is necessary to build artificial systems with good charge transfer efficiency and a long-lived charge separation state in order to improve the efficiency of energy conversion.[1-3]

Thus, we have developed donor-acceptor assemblies based on boron-dipyrromethene (BDY) as chromophore and electron donor and fullerene (C60) as electron acceptor. The photoinduced electron transfer process from $^1$BDY* to fullerene was confirmed by absorption, fluorescence, and transient absorption from femtosecond up to millisecond timescale. [4]

In order to investigate the potential of this dyad in the generation of photocurrent, these molecular systems were immobilized on gold surface by self-assembled monolayers (SAM) formation by attaching a helical hexapeptide that can be considered as surface structuring agent and a good electron mediator. The electrochemical and surface characterizations (XPS, QCM, and PM-IRRAS) of the SAMs show that the monolayers containing the peptidic chains are well packed and have a potential in photocurrent generation for photoelectrochemical devices. [5]

Scheme 1: a) Chemical structure of (C60-BDY) dyad peptide.


How Graphene and Hexagonal Boron Nitride get electrified in water?

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Abstract:
The recent emergence of nanofluidics has highlighted the exceptional properties of graphene and its boron-nitride counterpart as confining materials for water and ion transport [1-4]. Surprisingly ionic transport experiments have unveiled a considerable electrification of the water-BN surfaces, with a contrasting response for its water-carbon homologue [1]. This surface charging was conjectured to originate in the differential hydroxide adsorption at the surface of these twin materials, but the considerable challenge of simulating the elusive hydroxide ion has precluded a proper explanation up to now.

In this talk, we report free energy calculations based on ab initio molecular dynamics simulations of hydroxide OH⁻ ions in water near graphene and hexagonal boron nitride (h-BN) layers. Our results disclose that both surfaces get charged through hydroxide adsorption, but via strongly different mechanisms. The hydroxide species shows strong chemisorption on the h-BN surface, but only weak physisorption on the graphene surface [5].

Interestingly OH⁻ is accordingly shown to keep a very fast lateral dynamics and interfacial mobility in the physisorbed layer on graphene. This behavior sheds new lights on the experimental results on ionic transport in carbon channels. Taking into account the resulting large ionic surface conductivity, an analytical transport model allows to reproduce quantitatively the experimental data [5].

Our results offer new foundations for the chemical reactivity of carbon and BN materials in water and suggest new perspectives in the context of advanced membrane technologies for water purification and energy harvesting [6].

References:
5) B. GROSJEAN, M.-L. BOCQUET, and R. VUILLEUMIER, Submitted.
System level bistability of molecular Field-Coupled Nanocomputing

Yuri Ardesi, Mariagrazia Graziano, and Gianluca Piccinini

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Abstract:
Chemists and physicists have investigated and demonstrated through simulations the possibility of exploiting redox centers to aggregate charge in precise regions of oxidized molecules. This property allows the information encoding and enables the information transfer, via electrostatic interaction, through ordered sequences of molecules. This evidence makes the implementation of molecular Field-Coupled Nanocomputing (FCN) possible. The natural nanometric size of molecules and the absence of charge transport highlight molecular FCN as a possible technology for the future low power digital electronics. Our work consists in providing a methodology for the analysis, the design and the fabrication of molecular FCN devices, moving the focus from the single molecule, which has been already deeply discussed in the literature, to the molecular system. We develop an efficient model for studying systems of molecules organized as logic units, reducing the computational cost of ab initio simulations at the system level and keeping the chemical and physical properties of the assembled molecules.

More specifically in this work, we characterize the single molecule through DFT analyses and we use the results to analyze the capability of a molecular FCN wire to propagate digital information (Fig 1A). A self-consistent algorithm based on the aggregated charge (evaluated from the electrostatic potential surfaces) is used to model the electrostatic behavior of the molecules. It provides quantitative results about the information propagation and the energy associated with the electrostatic interaction among molecules (Fig 1B). We demonstrate the bistability of the molecular cell when inserted in a molecular system: it retains the digital information when the polarization of an input molecule is varied (Fig 1C). The bistability is enhanced by increasing the number of molecules in the wire and shortening the intermolecular distance (i.e. by strengthening the electrostatic interaction).

Figure 1. (A): molecular FCN wires, made up with bis-ferrocene molecules, propagating '1' and '0' bits. (B): Electrostatic Energy trend among molecules in a wire when polarizing (from RESET to HOLD state). (C): average polarization of cells in an FCN wire composed of 8 molecules with 1.0 nm intermolecular distance.

References:
Extending the applicability of Marcus theory in molecular junctions

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Abstract:
It is ultimately desirable for single-molecule technologies to operate at around room temperature. In these conditions it should be possible to describe the charge transport through single-molecule junctions [schematically pictured in Fig. 1(a)] using Marcus-type theories which treat the nuclear motion classically, and account for the electron-vibrational interactions through the overall reorganization energy, \( \lambda \). However, as we demonstrate here the conventional approach used in this context – Marcus-Hush-Chidsey (MHC) theory – gives rise to a number of artefacts resulting from (i) coupling to high-frequency vibrational modes (for which the high-temperature assumption of MHC is not justified), and (ii) the absence of lifetime broadening.\(^1\) We suggest alternative transport theories (still in the spirit of Marcus theory) which rectify the above shortcomings while largely retaining the mathematical simplicity of MHC approach.\(^1\) In particular, we derive a low-temperature correction to the semi-classical Marcus rates and show its importance in the resonant transport regime [Fig. 1(b)].\(^1\) Furthermore, we demonstrate how lifetime broadening can be incorporated into Marcus theory, and use this approach to describe the phenomenon of thermoelectricity in molecular junctions [Fig. 1(c)].\(^2\)

Figure 1: (a) Schematic of a fullerene-based molecular junction. (b) Resonant IV characteristics in the presence of electron-vibrational coupling calculated using various methods. (c) Seebeck coefficient calculated using the Landauer-Büttiker approach, Marcus-Hush-Chidsey theory and our approach.

References:

Halogen terminated self-assembled monolayers in molecular electronics – impact of backbone

Harshini V. Annadata, Xiaoping Chen, David A. Egger, Christian A. Nijhuis

Abstract:

Introducing halogen atoms into the backbones of self-assembled monolayers (SAMs) is an important step towards tuning intermolecular interactions by virtue of the molecular polarizability. However, predicting charge transport behaviour from polarizability from a text-book relationship is not straightforward. Here, we use density functional theory (DFT) with periodic boundary conditions to understand how work-function modifications and energy-level alignment of halogenated SAMs influence the device performance. We examine electrostatic and electronic properties of the molecular precursor and its corresponding SAM from both DFT and electrostatic modelling. Our results show that strategically terminating SAMs with halogens proved to be a particularly promising way to tune the dielectric and tunnelling rates of the SAMs. These findings are discussed in the context of effects that arise from the chemical nature of the backbone, and the role of effective mass of the tunnelling electron, while also being correlated to experimental data.

References:

Tuning of gold work function by carborane self-assembled monolayers using a Density Functional Theory

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Abstract:
Self-assembled monolayers (SAMs) act as tuners of surface properties useful for utilization in material research and nanotechnology[1,2]. Upon adsorption, the tuning of molecular level positions of SAMs composed of electronically active molecules occur and can be associated with the changes of the photovoltaic (PV) cells efficiency[3,4]. Carboranes among the SAMs building blocks attract attention due to a significant molecular dipole which can be oriented towards the surface or away from it. The investigation of the adsorption of carborane SAMs on Au(111) and resulting structures is performed through the first principle calculation based on a Density Functional Theory (DFT)[6]. The adsorption process is controlled by the electron density rearrangement from the surface gold layer to the sulfur anchoring groups of the carboranes leading to the Au-S chemical bond formations. These chemical bonds contribute to the dipole of the SAMs and thus also to the resulting work function (WF) changes that reach up to units of electronvolts (eV). Previous experiments using Kelvin Probe Force Microscopy (KPFM) showed a similar range of the WF changes which is sufficient for the change in the PV cells potential[5]. The resulting adsorption geometries strongly affect the final total energy. The minimal total energy is achieved at the slightly inclined geometry of the molecule relative to the surface. Such an arrangement can lead to a possible prediction of geometries generated during experiments.

Acknowledgement:
This work used facilities provided by TH02020628 project of the Technological Agency of the Czech Republic, project 17-27338Y of the Czech Science Foundation. Computational resources were provided by the National Grid Infrastructure MetaCentrum and the "Projects of Large Research, Development, and Innovations Infrastructures" program (CESNET LM2015042 and LM2015087).

References:
Transport properties of oligothiophene isomers

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Abstract:

We present here longitudinal electronic transport properties in linear polymeric oligothiophenes stranded between carbon nanotube and gold electrodes. In particular, the effect of bias, electrodes and isomerization of oligomers in the device on transport properties is investigated. These grafted oligothiophenes, are currently investigated in large area junctions and at the single molecule levels. The geometries of oligomers are optimized by means of the DFT/LCAO– S\(^2+\) vdW formalism, to take into account weak interactions. The probability of electron transmission in function of applied voltage is computed by using a non-equilibrium Green’s functions formalism [1,2]. The results are compared to recent experimental measurements [3].

References:


Carbon nanostructures for biosensing and biological energy conversion

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Abstract:

Due to the increasing need to monitor health and environment in real time and to energize small electronic devices, carbon nanotubes (CNTs) and graphene are, between other, promising alternatives as building blocks in bioelectrochemical devices due to their unique electrical, mechanical properties, biocompatibility and high specific surface. In the past years, we focused the development of biosensors and biofuel cells based on such carbon nanostructures [1-3]. Our efforts in this domain aim the construction of nano-architecture at molecular scale associating different nano-objects via organic or organo-metallic connectors to immobilize redox enzymes and bioreceptors [4-5]. Furthermore, our efforts focus redox enzyme wiring on nanotubes and graphene to enable efficient electron transfer with the electrode [2, 6].

The possibility to generate electrical power out of living organisms directed biofuel cell research towards glucose biofuel cells (GBFC) since the two required compounds (glucose and oxygen) are present in both, vegetal and body fluids [7]. However, in spite of this promising evolution, there are still too many issues to be resolved before enzymatic biofuel cells become competitive in practical applications. We follow the strategy to design GBFCs as an eco-friendly power source for disposable biomedical devices as alternative application where the proof of concept is presented [8].

References:

Cancer cell culture medium identification by super hydrophobic properties of organic electrochemical biosensor

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Abstract:
Conductive polymers demonstrate their ability as biosensor devices in Organic Electrochemical Transistors architecture. With sensible dependence in ions size, similar devices break down if challenged with complex mixtures, due to the lack of spatial resolution. Here, we modified a conductive PEDOT:PSS polymer to include extra non-continuous scales in the device. Super-hydrophobic SU8 pillars positioned on the substrate to form a non-periodic square lattice, allow increased super hydrophobic properties. Then a finite number of micro-electrodes produces a multiple local detection. The sample solution on device surface maintains a spherical shape. Main Marangoni convective flows could develop in the solution drop. The competition between convection and diffusion will cause a spatial separation of biological species, depending on the size and charge. Here we analyze the “waste deposit” of cell culture medium upon interaction with circulating cell isolated form peripheral blood sampling of health, sub-clinical and colon cancer patients. The analysis of culture medium, as an accessible source of biological markers, focuses on the concentration of positive ions. Understanding the cells metabolism, is a crucial topic to be useful for cancer early detection. Here, we demonstrate a super-hydrophobic organic electrochemical device may measure cell culture, showing significative differences between tumor and non-tumour patients. This assay could impact on cancer risk management, individual’s diagnosis and/or help clarify risk in healthy populations.

References:
Polymeric scaffold for wound healing monitoring based on biocompatible textile organic electrochemical transistor

Nicola Coppedè, Paola Losi, Andrea Zappettini, Marianna Buscemi, Tamer Al Kayal, Giorgio Soldani

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Abstract:

Recently, wearable devices have grown in importance, especially in healthcare, for their ability to collect crucial data, with noninvasive detection, to monitor patient’s physiological conditions. An emerging application is the monitoring of dangerous wounds, to detect the ulcer status. For chronic or infected wounds, the literature reports a pH interval between 6.5 and 9, with a high dependence on the healthy development of the wound. Our objective is to realize an innovative scaffold capable of monitoring ulcers healing, starting from high biocompatible materials to ensure a correct interaction with the physiology of the wound. The scaffold has been constituted by a synthetic biocompatible material, poly(ether)urethane-polydimethylsiloxane (PU-PDMS), was manufactured by spray, phase-inversion technique. This scaffolds has been successfully used in combination with fibrin as delivery system for VEGF, bFGF and platelet lysate in preclinical wound healing experiments. A micro-fibrillar tubular scaffold was obtained using a 1% polymer solution and H2O as non solvent (I layer) and 2% and H2O (II layer) and was lyophilized. The morphological analysis of PU-PDMS scaffold surfaces was performed by stereo-microscope after Sudan Black B staining, to ensure a correct shape surface interaction. The scaffold realized in such a way has been functionalized with a biocompatible conductive polymer (PEDOT:PSS), used as detector in Organic Electrochemical Transistor architecture. This polymer presents a high sensitivity to positive ions in liquid environment and allows to determine ions concentration in easy and stable way. The fiber textile electrochemical device has been realized by a dipping process and connected with specific electric contact to create a channel and a gate electrode to control the modulation changes of the sensor. The device functionality was proved on human serum at different pH (between 4 and 10). The morphological analysis showed a dense, non porous surface obtained with the 2% solution, while a porous surface was obtained with the 1% solution where the PEDOT:PSS was positioned. This feature was maintained after lyophilization and re-hydration. The characteristic of the device was tested showing the sensitivity to saline concentration and the effective functionality of the device. The device shows a sensitivity to pH change. The functionalized scaffold could be used as a wearable detector for wound healing monitoring in patients affected by chronic lesions.

References:

2 Sensors and Imaging for Wound Healing: A Review Tim R. Dargaville, Brooke L. Farrugia, James A. Broadbent, Stephanie Pace, Zee Upton and Nicolas H. Voelcker
POSTERS SESSIONS

Wednesday 19 December, 10:00 – 11:00
15:50 – 16:50
Influence of Intermolecular Interaction on Spontaneous Orientation Polarization in Evaporated Films of Organic Light-Emitting Diode Materials

Kohei Osada, Hisao Ishii, Yutaka Noguchi

Abstract:

Molecular orientation in organic films is very important because it influences the properties of organic light-emitting diodes (OLEDs) [1]. We have reported that spontaneous orientation polarization (SOP) is commonly observed in the evaporated films of OLED materials [2]. The surface potential of such films grows proportionally to their film thickness because of spontaneous order of permanent dipole moment (PDM) of the molecules. This phenomenon is known as giant surface potential (GSP) [3]. We discussed the relationship between GSP slope and PDM or intermolecular interaction and indicated the intermolecular interaction such as intermolecular hydrogen bond and dipole-dipole interaction may suppress SOP [2]. However, the formation mechanism and control method of SOP are still unknown. In this study, we measured GSP characteristics of the mixed film of polar and nonpolar molecules (TPBi and CBP, respectively) to investigate effects of the intermolecular interaction. We also examined GSP properties at hetero interfaces with varying substrate conditions.

Fig.1 shows the mixing ratio dependence of the normalized orientation degree of PDM and GSP slope in the mixed film of TPBi and CBP. Relationship of GSP slope (V/d) and PDM (p) can be described as V/d=n<cosθ>p/ε, where n is the density of polar molecule, ε is dielectric constant and <cosθ> is the average orientation degree of PDM with respect to the surface normal direction. Interestingly, the GSP slope shows nearly constant in the mixed films, that is, orientation degree of PDM is increased with decreasing mixed ratio of TPBi. Since co-evaporation with CBP increases the intermolecular distance between TPBi molecules, dipole-dipole interaction decays in the mixed film. As the result, the probability that PDMs cancel each other may be reduced and the orientation degree is enhanced.

We also measured the local potential distribution of the TPBi film on the Au substrate with/without 1-Dodecanethiol self-assembled monolayer (SAM) by using Kelvin probe force microscopy. A relatively small surface potential was observed near the boundary between the TPBi film and the SAM treated substrate. The weak interaction with the substrate may induce the molecular packing of TPBi with reducing electrostatic energy, consequently SOP.

References:


Towards single POM photoswitch for data storage

Michele Mattera, Imad Arfaoui, David Kreher, Anna Proust, Florence Volatron

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Abstract:

In this actual era of fast technological advances, the need for more powerful computers and denser memories contrains to push further the limits of the traditional electronics, going down to the molecular level. Polyoxomometalates have remarkably electronic properties which makes them good candidates, as molecular components for data storage, since they have already been exploited in flash memory devices.\(^1\)

The Keggin family of phosphomolybdates with different alkylammonium-based counter cations will be studied (see Fig 1a).\(^2\) Interestingly this family can be reduced in the presence of an UV light, without any external reducing agent.\(^3,4\) This process is reversible and could be exploited to program these polyoxometalates, and the reading process can take place by applying a small bias current.

Because we want to use each polyoxometalate as a bit of information, we will show how is it possible to work at the sub monolayer level, by isolating each cluster from each other, covering areas in the order of the centimeter square. The successful isolation is obtained by using a porous bidimensional network, based on aromatic stilbene units, that will immobilize and host the clusters, by means of hydrophobic weak interactions (see Fig 1b). Depending on the side chains present on the stilbene units, the network can adjust itself to the guest that want to accommodate.\(^5,6\)

We studied different parameters in order to optimize the overall coverage of the surface: the concentration of the POM, the solvent used, the pore diameter of the network and also the deposition method.

Figure 1 - a) Example of Keggin Family Phosphomolybate with alkylammonium counter cation. b) Bidimensional aromatic stilbene-based porous network.

References:

Large-area Thermoelectric Junctions Formed with Eutectic Gallium-Indium Electrode

Sohyun Park, and Hyo Jae Yoon*

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Abstract:
A challenge in organic thermoelectrics is to relate thermoelectric performance of devices to the chemical and electronic structures of organic component inside them on a molecular scale.\(^1\)\(^2\) To this end, a reliable and reproducible platform relevant to molecular-level thermoelectric measurements is essentially needed. This paper shows a new, efficient approach for thermoelectric characterization of large-area of molecular monolayers using liquid eutectic gallium-indium (EGaIn). Cone-shaped EGaIn\(^3\) microelectrode permits access to non-invasive, reversible top-contact formation onto organic surfaces in ambient conditions, high yields of working devices (up to 97%), and thus statistically sufficient thermoelectric data sets (~6000 data per sample in a few hours). We here estimated thermopowers of EGaIn (3.4 ± 0.1 μV/K) and the Ga\(_2\)O\(_3\) layer (3.4 ± 0.2 μV/K) on the EGaIn conical tip and successfully validated our platform with widely studied molecules, oligophenylenethiolates. Our approach will open the door to thermoelectric large-area molecular junctions.

References:
Effects of ionic liquid layers on morphologies, structures and electrical properties of thin films of pentacene and fullerene

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b Furo-cho, Chikusa-ku, Nagoya, Department of Chemistry, Nagoya University, Japan.

Abstract:
Ionic liquids (ILs), which consist of mobile cations and anions, and hybrid IL and polymer materials have been used as gate dielectric materials in OFETs to accumulate a high carrier density (ca. $10^{15}$ cm$^{-2}$) in the active layer due to their high capacitances [1,2]. These specific properties originate from their mobile characteristics and the formation of electrical double layers (EDLs) at the electrified solid-IL interfaces [1]. However, these properties of ILs are known to break down under confined conditions, resulting in the formation of characteristic structures and orderings, which are quite different from those of bulk ILs [3]. In this work, we investigated the effects of an IL, $N,N$-diethyl-$N$-methyl-$N$-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME–TFSI, Fig. 1a), sandwiched between substrates and organic layers, on the morphologies, structures, and electrical properties of thin films of organic layers.

DEME-TFSI was deposited on the FET substrates with a bottom gate, bottom-contact-device architecture having $\text{SiO}_2$ insulating layers (300 nm) thermally grown on highly doped n-Si substrates (gate electrodes) and comb-shaped Pt electrodes (width/length = 7.9 cm/20 $\mu$m). Subsequently, the thin films of pentacene (10 ML) were prepared on the substrates without exposure to air (Fig. 1b). FET measurements were performed in situ under high vacuum conditions without exposure to air at room temperature in the dark, using a source-measure unit (Advantest Corp. R6245A). Ex situ structural and morphological characterization were performed for the thin films under ambient conditions using an X-ray Diffractometer (XRD) and an atomic force microscope.

The thin films of pentacene prepared on IL-coated Si substrates exhibited dendritic structures but the growth of dendritic structures was strongly suppressed on the DEME–TFSI layers. The XRD of the thin film of pentacene on the bare substrate showed a peak at $2\theta = 5.7^\circ$, which corresponds to the (001) plane of the thin-film phase of pentacene. The intensity of the peak decreased with the thickness of the DEME–TFSI layers. In addition, an additional peak corresponding to the bulk phase was observed in the XRD of the thin film on 5 ML DEME–TFSI. The pentacene FET without the DEME–TFSI layer exhibited a typical p-type channel behavior with a small hysteresis loop, while the pentacene FETs with the DEME–TFSI layers displayed p-channel behaviors with larger hysteresis loops. The size of the hysteresis showed a dependence on the thickness of the DEME–TFSI layers. The OFETs with the DEME–TFSI layers has the potential for use in memory devices.

References:
Organic-inorganic thin multilayer for organic light emitting diode passivation film by a single deposition chamber

Yoonseuk Choi, Min-Hoi Kim, and Jae-Hyun Lee

Abstract:
We investigated poly-para-xylylene (parylene) and Aluminium Nitride (AlN) multilayer thin film as passivation for organic light emitting diodes (OLED), fabricated in a short process time at room temperature using a single deposition chamber. We deposited the parylene and AlN layers using an optimized chemical vapor deposition technique and sputtering respectively. The passivation film has an optical transmittance of 90%. Moisture barrier performance was improved with increasing thickness and number of layers. OLED devices with half-life of 30 hours passivated with Parylene(6.4μm)/AlN(50nm)/Parylene(0.6μm)/AlN(50nm)/Parylene(0.6μm)/AlN(50nm) films showed preserved shelf-life, in excess of 48 hours under 37.8 °C and 90% RH conditions.

Figure. Schematic diagram of a single system for multilayer passivation thin film deposition

Acknowledgement:
This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20183010013840)
Tunneling-Based Access Resistance in Layered Single-Crystal Organic Semiconductor

Takamasa Hamai, a Shunto Arai, a Hiromi Minemawari, b Satoru Inoue, b, c Tatsuo Hasegawa a, b

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Abstract:
Organic thin film transistors (OTFT) are the key component of flexible and printed electronics with its processability under room-temperature and ambient pressure. Recent studies revealed that π electron core substituted by long alkyl chain shows optimal characteristics such as high layered crystallinity, solubility to conventional organic solvent, and high carrier mobility. However, a potential problem which comes from the insulating nature of substituted alkyl chains are not elucidated.

Here, we report the effects of vertical tunnel transport across alkyl-chain layers in single-crystal OTFT of Ph-BTBT-C10 [1, 2]. In OTFTs with staggered geometry (Fig. A), ohmic contact in ultrathin films systematically changes to highly nonlinear contact with the increase of the layer number (n) (Fig. B). The device mobility is also layer-number-dependent: The device mobility in linear regime of thick film with n=15 (~80 nm thick) is 5 times smaller than that of ultrathin film with n=2 (10.6 nm thick) (Fig. C). These drastic change of device characteristics were reproduced by numerical calculation with a simplified model which assumes that the nonlinear access resistance is derived from tunneling conduction across the alkyl-chain insulating layers. We also experimentally confirmed that the vertical transport is dominated by tunneling by measurement with template-stripped Au (AuTS) and eutectic gallium indium (EGaIn) electrodes (Fig. D) [3]. In the presentation, we discuss the completely different two carrier conduction mechanism in intra-layer and inter-layer transport in Ph-BTBT-C10.

References:
The Role of Molecule–Electrode Interfacial Defects in Large-Area Tunneling Junctions

Hyunsun Song\textsuperscript{a}, Gyu Don Kong\textsuperscript{a}, Junji Jin\textsuperscript{a}, Martin Thuo\textsuperscript{b}, Joonyoung F. Joung\textsuperscript{a}, Sungnam Park\textsuperscript{a}, and Hyo Jae Yoon*\textsuperscript{a}

\textsuperscript{a} Department of Chemistry, Korea University, Seoul 02841, Korea, hyoon@korea.ac.kr
\textsuperscript{b} Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, United States

Abstract:

Herein, we compare two analogous junctions formed with identical organic thin film and different liquid top-contacts (water droplet vs eutectic gallium indium alloy\textsuperscript{[1]}) and elucidate the puzzling interfacial characteristics. Specifically, we fine-tune the surface topography of the organic surface using mixed self-assembled monolayers (SAMs)\textsuperscript{[2]}: single component SAM composed of rectifier (2,2′-bipyridyl-terminated n-undecanethiolate; SC\textsubscript{11}BIPY\textsuperscript{[3]}) is systematically diluted with nonrectifying n-alkanethiolates of different lengths (denoted as SC\textsubscript{n} where n = 8, 10, 12, 14, 16, 18). Characterization of the resulting mixed SAMs in wettability and tunneling currents with the two separate liquid top-contacts allows us to investigate the role of phase segregation and gauche defect in the SAM/liquid interfaces. The results reported here show the difference in length between SC\textsubscript{11}BIPY and SC\textsubscript{n} translated into nanoscopic pits and gauche-conformer defects on the surface, and the difference in contact force—hydrostatic vs user pressures—and hence conformity of contact account for the difference in wettability and rectification behaviors. Our work provides an insight into the role of molecule–electrode interfacial defects in performance of molecular-scale electronic devices.

References:

Understanding Cross-Conjugation for Organic Electronics

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Abstract:

π-Conjugated organic molecules have been the focus of interest since they have been probed as potential semiconducting materials, suitable for replacing the widely used silicon technologies. Their structural, optical and conductive properties are now under study to improve their application in organic electronics and to make possible their ad hoc synthesis. In this sense, the knowledge of the π-electron delocalization is crucial to establish the relation between the properties and the function, enabling the development of a synthesis guide based on the specific application.

The most acknowledged conjugated organic materials are those which present extended, linearly-conjugated π-systems. However, this is not the only way of π-electron delocalization: homoconjugation, cross-conjugation, curved-conjugation, etc. constitute different electronic designs to achieve new organic materials.

There is a relative high abundance in the organic world of cross-conjugated but limited comprehension. Thus, the understanding of how cross-conjugation works in π-electronic systems is of importance. Following this idea, in this project we show 4 different structures which present two perpendicular π-conjugated paths and how the cross-conjugated property is revealed. On the one hand, two molecules based on thieno[3,4-c]pyrrole-4,6-dione quaterthiophenes allow us to accomplish the subject from the aromatic/quinoidal outlook, and, on the other hand, two molecules with an anthanthrone core make possible the study from the perspective of the substituent groups.

Cross-conjugated paths in a quaterthiophene-based molecule.

References:

Electrochemical surface modification for the modulation of electrical properties of organic devices

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Abstract:

Organic electronics is a field of intensive research thanks to the diversity of molecular structures reachable by organic synthesis. Molecular materials offer convenient shaping processes, such as solution processing techniques, which can be used for the fabrication of organic devices on plastic substrates.

We present the elaboration of two original conductometric devices: a conductometric gas sensor called MSDI heterojunction\(^1\) and a polymer – phthalocyanine double lateral heterojunction. The properties of these devices are highly dependent on the interfaces. Electrochemistry was used both to modify the electrode surface of the MSDI and to synthesize the polymer.

\[\text{modified CuF}_{16}\text{Pc} - \text{LuPc}_2 \text{ n-MSDI} \]

\[\text{Polymer} - \text{LuPc}_2 \text{ double lateral heterojunction} \]

We studied the impact of the electrode surface modification on the electrical and sensing properties of the devices.

Previous works on the development of MSDI emphasized the primary role of interfaces, particularly in the case of n-MSDI that contained a p-n heterojunction. We grafted different substituted benzenes by reduction of the corresponding diazonium salts on interdigitated electrodes. The various surface modifications mainly acted as an insulating barrier that amplified the nonlinear behavior of the current-voltage characteristics of MSDI. The grafting of 2,5-dimethoxybenzene significantly improved the ammonia sensitivity of MSDI based on copper hexadecafluorophthalocyanine and lutetium bisphthalocyanine, with a limit of detection of around 200 ppb.

We also developed polymer - phthalocyanine lateral heterojunctions based on polyaniline or substituted polyanilines having either electron withdrawing, the poly (2,3,5,6-tetrafluoroaniline)\(^2\), or electron donating groups, the poly (2,5-dimethoxyaniline). Their electrical behavior, studied by impedance spectroscopy and the record of the I(V) characteristics, differs according to the nature of the substituents of the electrodeposited polyaniline. Their sensing measurements revealed their efficiency to detect ammonia in humid atmosphere, with a sub-ppm limit of detection.

References:


Ag nanoparticles for application to electronic device materials

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Abstract:
In recent years, metal nanoparticles have been paid much attention, which have various and superior characteristics. The materials, including gold, silver and copper, can be applied to the fabrication of nano inks. Those are especially worthy of method to fabricating electronic devices. By coating or inkjet printing of metal nano ink, a dense circuit can be drawn on a small electronic substrate. It can also be fabricate a multilayer device by using metal nano ink with conductive polymers, organic EL materials. In this study, we report the simple method for preparation and properties of silver nano ink.

The method for preparation of metallic nano ink was developed by Fect Inc. It uses a common silver oxide as a precursor. Although an unusual solvent and a polymer dispersant (surfactant) are required, the method is a very simple. TEM image of silver nanoparticles contained in the silver nano ink obtained by this method is shown in figure 1. The particle size of silver nanoparticles were relatively uniform at around 50 nm, and it can be confirmed that they were uniformly dispersed. These silver nano particles were covered with a polymer dispersant (surfactant) used in the process for preparing of silver nanoparticles. Therefore, when this silver nano ink is applied, it has a beautiful silver metallic luster, however the silver nano layer did not exhibit electroconductivity.

A polymer dispersant (surfactant) can be easily removed by linsing with a common solvent. TEM image of silver nanoparticles contained in the silver nano ink obtained after linsing process method is shown in figure 2. The particle size of silver nanoparticles was relatively growing. It can be confirmed that they are aggregated and are stripped off a polymer dispersant (surfactant). Thus, the silver nano layer, which is fabricated from new silver nano ink, has both of a beautiful silver metallic luster and electroconductivity.

Fig.1 TEM image of silver nanoparticles with the surfactant.
Fig.2 TEM image of silver nanoparticles with no surfactant.
A study of leakage current behavior according to blade-coating velocity in a metal-polymer dielectric-metal capacitor

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Abstract:

Solution process of organic electronic materials have attracted significant attention for their potential of flexible and large-scale electronics in low-cost [1]. Among many solution coating techniques, meniscus-guided coating have been actively studied due to easy controllability of thickness and electrical characteristics in large-scale [2]. However, many researches have been focused on semiconductors to improve field-effect mobility of transistors, and less attention has been paid to the dielectrics even though dielectric properties highly effect on leakage current and operational voltage of capacitor or transistor [3]. Therefore, understanding of relationship between coating parameters and electrical characteristics of dielectric film in meniscus-guided coating is essential for large-area, high-performance organic electronics.

Here, we demonstrate the leakage current behavior according to coating velocity which is one of the major parameters in meniscus-guided coating method in a metal-polymer dielectric-metal capacitor structure. The representative polymer insulator, cross-linkable poly(4-vinyl-phenol) (c-PVP) was blade-coated at the speeds of 2, 5, and 10 mm/s over a large indium-tin-oxide coated glass substrate (10x10 cm²) as shown in Fig. 1(a) to fabricate metal-insulator-metal capacitors. The current density was measured in electric field range of 0 - 1.2 MV/cm as shown in Fig. 1(b). The current densities for the coating speeds of 2, 5, and 10 mm/s at the electric field of 0.3 MV/cm were 8.3x10⁻⁵, 1.6x10⁻⁶, and 1.4x10⁻⁵ A/cm², respectively. The capacitor with c-PVP coated at the speed of 5 mm/s shows the lowest leakage current density regardless of the electric field.

![Diagram](image_url)

Figure 1. (a) Schematic of blade-coated metal-polymer dielectric-metal capacitor and (b) current density of fabricated capacitors as a function of electric field.

References:

Computational Design of Novel Organic Semiconductors

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Abstract:

Small-molecule organic semiconductors are used in a wide spectrum of applications, ranging from organic light emitting diodes\cite{Groves13} to organic photovoltaics. A number of factors determine mobility, such as molecular packing, electronic structure, dipole moment and polarizability. Presently, quantitative ab-initio models to assess the influence of these molecule-dependent properties, including the influence of dopants, are lacking. Here, we present a multi-scale model, which provides an accurate prediction of experimental data over ten orders of magnitude in mobility \cite{Friederich16}, and allows for the decomposition of the carrier mobility into molecule-specific quantities. The model consists of a multi-step procedure, incorporating single molecule parameterization, generation of atomistic morphologies,\cite{Neumann13} DFT based electronic structure calculations yielding site energies, energy disorder, electronic couplings and reorganization energies.\cite{Friederich14} These parameters are used in an analytic model\cite{Rodin15} to compute the charge carrier mobility of the amorphous materials. We also provide molecule-specific quantitative measures how two single molecule properties, the dependence of the orbital energy on conformation and the dipole induced polarization determine mobility for hole-transport materials. On the basis of this methodology we are able to computationally predict novel pure ETL materials with three orders of magnitude higher mobility than their precursors \cite{Friederich17} and elucidate the molecular mechanism of doping these materials with kinetic Monte-Carlo simulations. The availability of first-principles based models to compute key performance characteristics of organic semiconductors may enable in-silico screening of numerous chemical compounds for the development of highly efficient opto-electronic devices.

Rapid access to organic semi-conductors based on benzodifurane/thiophene for OPV applications

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Abstract:
Organic semiconductors (OSC) are the basis for the development of plastic electronics whose applications are linked to LED displays systems, to low voltage lighting (white light emission), to microelectronics (field effect transistors) or to solar energy (photovoltaic cells) conversion [1]. In the context of clean energy, access to organic semi-conductors should be very rapid (few steps) and based on green synthetic methods [2] such as cycloaddition reactions (atom economy), condensation reactions (only water as waste), cascade reactions or direct arylation reactions (atom economy). We have used these methodologies to build organic semi-conductors containing donor-acceptor groups to tune electronic levels. First examples were based on direct arylation of substituted thiophenes to afford donor-acceptor-donor (D-A-D) materials [3]. Other examples consist of benzodifurane moieties [4] from which donors and acceptors have been linked by condensation reactions. The electronic properties of the different compounds have been studied, and some solar cells have been realized.

References
Electronically conductive polymers in electroanalytical chemistry: from potentiometric to biologic gates

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Abstract:
Electronically conductive polymers represent an interesting class of materials for the design of electroanalytical tools owing to their intrinsic electrical/electrochemical properties and doping behavior. More particularly, our attention was devoted to the design of low cost and accurate electrochemical (bio)sensors that could be implemented for example in point of care devices for patient survey at home or in pathogen detection in food using molecular biology principles.

Screen printing technology is a very efficient process for the high rate fabrication of electroanalytical systems. Moreover, electronically conductive polymers such as Polyaniline and PEDOT are now commercially available as screen printable inks. In such a context, we developed printed potentiometric sensors and organic electrochemical transistors (OECT) for the selective detection of metabolites in complex media.

First PANI based pH electrodes were developed for the monitoring of isothermal polymerase chain reaction (PCR LAMP). We recently shown the possibility to detect accurately 10 copies/mL of bacterial DNA in less than 30 min using a \textmu{}fluidic PCR reaction chambers embedding PANI pH electrodes\textsuperscript{1}.

Secondly, we demonstrated the possibility to develop printed OECT with similar performances than classical lithographed systems using screen printed PEDOT inks. We first focused on the development of fully printed biosensors for lactate and glucose\textsuperscript{2}. But, away from classic biosensing, OECT offer the unique possibility to be combined for the design of more complex electronic circuitry. Thereby, some basic electronic architectures, Wheatstone bridge, as well as NAND and NOR gates, were designed. The former circuit was implemented for the referenceless measurement of pH in sweat\textsuperscript{3}. An original NOR gate was finally assayed for the design of an enzymatic logic gate using lactate and glucose as input signals.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{referenceless_pH_measurement.png}
\caption{Referenceless pH measurement using OECT based Wheatstone bridge. (a) Layout of the sensing function and picture of the device. (b) Drawing of the pH evolution in the two wheatstone bridge chambers and differential pH and recorded output signal.}
\end{figure}

References:
\textsuperscript{1}Gosselin et al, Anal. Chem. 2017, 89, 10124–10128
\textsuperscript{2}Scheiblin et al, MRS Commun. 2016, 5, 507-511
\textsuperscript{3}Scheiblin et al, Adv. Mater. Tech 2016, 2, 1600141
Water-Gated Organic Field-Effect Transistors: Biosensing Applications

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Abstract:

In the field of organic transistors, Electrolyte-Gated OFETs have recently emerged, where the classical dielectric of an OFET is replaced by water. Polarization of the gate causes formation of an electrical double layer (EDL) at both the gate/water and semiconductor/water interfaces, causing accumulation of carriers in the semiconductor, thus a drain current ($I_D$) increase. Due to the extreme thinness of the EDLs, operating potentials are of a few hundreds of mV only. It is known, for classical OFETs, that $I_D$ depends on the dielectric capacitance. Interestingly, for a water-gated OFET, the overall capacitance depends on two interfaces: the organic semiconductor/water and the water/gate capacitances.

As a consequence, physicochemical processes occurring at the water/gate interface, such as changes in interfacial capacitance induced by molecular recognition of a target molecule onto an immobilized receptor, or accumulation of ions, can be transduced and, most importantly, amplified into a drain current variation. This paves the way for applications in the field of biosensors.

At first in this work, we will focus on different methods able to biofunctionalize the semiconductor interface, which is challenging because covalent or even non-covalent functionalization of semiconductors led to significant degradation of charge carriers' mobility. For applications such as immunosensing, we will show that gate modification is pertinent and that microelectrodes or even ultramicroelectrodes can gate such organic transistors. Two approaches of gate functionalization and two transduction mode will be illustrated, with practical examples such as selective detection of small organic molecules or even ions in water.

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Abstract:
Since the first reported synthesis of a cycloparaphenylene (CPP) by R. Jasti et al in 2008, 1 many nanorings made of various units such as fluorene, naphthalene or stilbene have been synthesized and studied. This type of cyclic nanostructure arouses a large keen interest because of their unexpected properties. For example, in linear oligophenlenes, we observe a decreasing of the HOMO-LUMO gap while increasing the number of phenyl units, whereas the HOMO-LUMO gap of the CPPs increases with the size of the ring (and the number of phenyl units). Considering that linear organic semi-conductors are the molecular pillars which have allowed the development of organic electronics, investigating their cyclic counterparts appears as an exciting challenge. Thanks to its appealing properties (particularly its electron rich character), the carbazole fragment has been widely used in the design of functional materials for organics electronics and appears therefore as an interesting building unit to construct nanorings. The first examples of cyclocarbazoles have been reported by Yamago et al in 2016. 2 In these examples, nitrogen atoms were substituted with methyl and phenyl groups and this work mainly concerned the ring currents induced by the peculiar cyclic geometry. In this present work, we report an improved synthesis of a cyclocarbazole nanoring including four carbazole fragments possessing nitrogen atoms substituted with ethyl chains. The electrochemical, photophysical and their interplay will be detailed and rationalized thanks to molecular modelling. Thus a redox-fluorescent switch will be presented. Incorporation of [4]cyclo-9-ethyl-2,7-carbazole in an organic field-effect transistor (OFET) is finally presented. As organic devices based on nanorings are barely explored to date, this work shows that nanorings can be successfully introduced as an active layer in an OFET but also provides a first benchmark for nanorings.

Figure 1. (left) X-Ray crystal structure of [4]cyclo-9-ethyl-2,7-carbazole and (right) UV-Vis absorption (solid line) and emission (dashed line) at RT in cyclohexane

References:
2. L. Sicard, O. Jeannin, J. Rault-Berthelot, C. Quinton; C. Poriel, chempluschem, 2018, 83, 9, 874
Air stability of p-doped organic semiconductors: can they be processed under ambient conditions?

Tamara Nunes Domschke, Alexandre Pereira, Raphael Clerc, Alexandre Carella and Anass Benayad

Abstract:
Chemical doping allows tuning the electrical and optoelectronic properties of organic semiconductors (OSC) and conductive polymers, offering a promising solution for improving the electrical contact quality of organic electronic devices. However, controlled and efficient doping of OSC by solution-processed methods remains challenging. In addition, in order to be adapted for large-scale printing and patterning techniques, these doped layers should be stable to short periods of air exposure. Depending on their energy levels, organic materials can undergo redox reactions with water and/or oxygen species from ambient air. For example, it is well known that n-dopants are susceptible to suffer from immediate oxidation in air due to their low ionization energies (IE), compromising the air stability of n-doped OSCs. In contrast, efficient p-dopants are supposed to be air-stable molecules thanks to their high IE (> 5eV), but the stability of p-doped OSCs has never been investigated in detail so far.

Here, we study the impact of the processing atmosphere (air vs. N₂) on the p-type doping of the low bandgap polymer poly[(4,8-bis-(2-ethylhexyloxy)benzo(1,2-b:4,5-b’)-dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl)] (PBTTTT-c) with the molecular dopant tris[1-(trifluoroethanoyl)-2-(trifluoromethyl)ethane-1,2-dithiolene] (Mo(tfd-COCF₃)). For p-doped layers prepared in inert atmosphere, the conductivity increased over six orders of magnitude. First, we report on an anomalous thickness dependency of the conductivity observed for the air-processed layers, which increased over two orders of magnitude with the layer thickness (varied from 15 - 200nm). This behavior was not present in N₂-processed doped layers. Hence, air-processed PBTTTT-c:Mo(tfd-COCF₃) layers showed a conductivity drop over time. Additional ageing experiments carried out under different atmospheres (nitrogen, anhydrous air, air) indicated that humidity plays a major role in the observed degradation mechanism.

In a second part, X-ray photoemission spectroscopy (XPS) allowed us to demonstrate that once in the p-doped system, Mo(tfd-COCF₃) is prone to oxidation under ambient conditions. In conclusion, our results highlighted an unexpected air instability of thin p-doped layers, opening the field for future investigations.

References:
High Thermoelectric Harvesting From Ionic Conductive Polymer

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Abstract:
Thermoelectric effect of conductive polymer films were explored by controlling the dopant content for poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). Highly doped conductive polymer films were synthesized in the presence of high molecular weight PSS under an optimized temperature and humidity. As prepared polymer films showed high Seebeck coefficient and ionic conductivity, which led high power factor of thermoelectric conversion. Simultaneously, it showed large electrochemical and thermal capacitance due to the mixed ionic carriers. Surprisingly, the thermal charging afforded a high thermal voltage and current output, reproducibly, to show thermocapacitive properties in the absence of external capacitors. This suggests that such proton transport in TE materials represent a new way to exceed the limitations of traditional TE harvesters, including electronic, ionic, or mixed ionic thermoelectric harvesters, and it could be useful for body-worn or hand-held electronics.

Figure. Thermovoltage at different ΔT and 90% RH. The slope of the linear fitting to the data for the Seebeck coefficient.

References:
Towards the fabrication of all-inkjet-printed, flexible Electrolyte-Gated Organic Field-Effect Transistors

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Abstract:

Electrolyte-Gated Organic Field-Effect Transistors (EGOFETs) have recently attracted considerable attention. The very low biasing potentials (< 1 V) and the possibility of employing fast-response polymer electrolytes make EGOFETs ideal candidates for the next generation of electronic switches and amplifiers.[1] At the moment, the large majority of EGOFETs reported in the literature were fabricated on rigid substrates with extensive use of clean-room photolithographic processes.[2] These factors clearly limit the transistors portability and also considerably increase the cost per device. Surprisingly, the utilisation of the inkjet-printing (IP) technique for the fabrication of EGOFETs has received up to now little attention: no examples of fully inkjet-printed EGOFETs on flexible, plastic substrates have been described so far. In this communication, we report on the fabrication of fully inkjet-printed EGOFETs, realised on flexible, plastic substrates (namely Kapton®). The first part of the presentation will be devoted to the formulation and rheological characterisation of semiconducting inks, inkjet-printed on source and drain electrodes fabricated by means of photolithography on silicon wafers. After demonstrating the feasibility of printing the semiconducting layer (Fig. 1a), the second part of the talk will be focused on the inkjet-printing of the source, drain and gate electrodes, using an original, coplanar configuration where the three electrodes lie on the same plane (Fig. 1b). Inkjet-printed EGOFETs were electrically characterised in terms of output and transfer curves and the most important electrical figures of merits were extracted (Fig. 1c). Our results could pave the way for the fabrication of the next generation of low-cost, flexible and portable printed circuits and devices.

Figure 1. (a) Inkjet-printed organic semiconductor; (b) detail of inkjet-printed electrodes on Kapton; (c) output curves of the transistor shown in (a).

References:
Characterization of Memristor Behavior based on TiO$_2$/TiO$_{2-x}$ Layers

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Abstract:
For several decades the size of transistors has been continuously decreasing as a result of advances in digital electronics as expressed by Moore’s Law, and innovation has ultimately pushed CMOS technology to the 12-nm feature width that presently exists [1,2]. In this work, we have investigated the effect of the thickness of the oxide active layers with device architecture of Al (top electrode)/TiO$_2$/TiO$_{2-x}$/ heavily doped bottom electrode for the behavior of memristor. TiO$_2$ insulating thin film was deposited using ALD system and TiO$_{2-x}$ active layers were deposited at 5 nm, 10 nm, and 15 nm by an RF sputtering system. When the electrical characteristics of the memristor were observed, the memristor based 10 nm thick active layer is exhibited the most complete hysteresis curve at the I-V curve applied -3 to 3 V. A As the surface with 10 nm thickness was analyzed with atomic force microscopy, it is noted that the roughness was small and the grain boundary was clear. In addition, the electrical characteristics of nonvolatile memory were confirmed by measuring the retention stability.

Fig. 1 Schematic representation of TiO$_{2-x}$/TiO$_2$ based memristor device.

Fig. 2 ON/OFF ratio and AFM image of the memristor with TiO$_{2-x}$ layers of (a) 5 nm, (b) 10 nm, and (c) 15 nm.

References:
Multi-Layer Stacked Indium Zinc Oxide Thin-Film Transistors with Femtosecond Laser Post-Annealing Treatment

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Abstract:

Post-annealing process is a reliable and effective treatment in active film fabrication, it has greatly affected on surface shape and roughness of indium zinc oxide (IZO) thin-film and low surface roughness may improve the electrical properties of thin-film transistors (TFTs) [1,2]. In this research, the three-layer active film stack IZO TFTs with femtosecond laser post-annealing process treatment, so as to investigate of the post-annealing treatment with femtosecond laser of multi-layer active film stack IZO TFTs on the electronic properties. The multi-stacked IZO TFT exhibited field-effect mobility of approximately 5 cm²/Vs and current on/off ratio of approximately 2 × 10⁶, especially the electrical performance after 14 days still maintains a decent status with field-effect mobility of approximately 4 cm²/Vs and current on/off ratio of approximately 2 × 10⁴. The experimental results of electrical properties show that the voltage gain, switching response and electrical properties of IZO TFTs with femtosecond laser post-annealing treatment were significant improved. In particular, the TFTs with post-annealing process treatment by femtosecond laser for 100 s has good stability and still maintains good electrical properties after several weeks.

Fig. 1 Schematic representation of the three-layer active film stack IZO TFTs structure

Fig. 2 Output characteristic curves of IZO TFTs after 0 s, 50 s, 100 s, and 200 s femtosecond laser post-annealing process treatment.

References:

Comprehensive Analysis of Indium Zinc Oxide Thin Film Transistor with Multi-layers Active Film Stack Structure

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Abstract:
Indium zinc oxide (IZO) thin film transistor (TFT) has the advantages of exceptional field-effect mobility, large on–off current ratio ($I_{on}/I_{off}$), exceptional uniformity, excellent light transmittance and outstanding electrical stability [1]. In recent years, it has been used more in fabrication process of the Thin Film Transistor. With continuous development, the IZO TFT with multi stack active layer structure is detected decent electronic performance than single active layer TFT [2]. Multi-IZO-layer is proposed as a new active film stack structure for more optimized electrical performance of IZO TFTs. The surface roughness of thin film formed by multi-IZO-layer was measured by using Atomic Force Microscope (AFM), giving a low root-mean-square (RMS) roughness of 0.465 nm. Compared with the single layer (RMS = 0.695 nm), it has smaller folds and a smoother surface. The results show that the multi active layer TFT is higher than single active layer TFT as shown in field-effect mobility of $7.75 \pm 0.2$ cm$^2$/V·s, threshold voltage($V_{th}$) is $0.35 \pm 0.42$V, and light transmittance stable at more than 85 percent. Consequently, the electrical characteristics are improved by multi-layers active film stack structure of IZO TFTs, and the multi-IZO-layer is a promising structure for next-generation semiconductor devices that simultaneously can improve electrical characteristics and stability.

Fig. 1 Schematic representation of Multi Stacked Structure IZO TFT.

Fig. 2 (Color online) AFM topographies and cross sections for single layer and multi layer thin film.

References:
New high triplet energy 2,7-dimethoxycarbazole-based materials for blue organic light-emitting diodes

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Abstract:

Nowadays organic light emitting diodes (OLED) are gaining more popularity in the global market as an alternative for LED. The use of thermally activated delayed fluorescence (TADF) is a promising approach to efficient blue electroluminescence. Improving the performance of blue organic light-emitting diodes electrochemically and thermally stable materials are needed, as well.

Since Adachi et al. [1] synthesized D-A-D emitters for efficient blue TADF OLEDs based on carbazole and diphenylsulfone, in our work, we designed and synthesized various new compounds using newly designed carbazole moieties, such as 2,7-dimethoxy-3,6-di-tert-butylcarbazole and 2,7-dimethoxy-3-tert-butylcarbazole (Fig.1). It is known that 2,7-substituted derivatives of carbazole show irreversible oxidation. [2] Therefore, we introduced tert-butyl groups to obtain higher thermal and electrochemical stability. All compounds have been investigated using density functional theory and the comparative experimental study was performed. Due to very small theoretical/experimental singlet-triplet energy splitting (~0.1-0.2 eV) new D-A-D molecules were analyzed as potential candidates for thermally activated delayed fluorescent effect.

References:

Quinoline and carbazole based materials for non-doped white OLEDs

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Abstract:
Bipolar conjugated molecules with donor-acceptor architecture are of great interest of scientists due to its wide potential application in optoelectronic devices. A significant interest has focused on development of white organic light emitting diodes (WOLEDs), as possible low-cost, highly efficient alternatives for back-lights in flat panel displays 1. Tunable combination of two or three exciplex systems affords simple way to obtain efficient white light emission 2.

We designed and synthesized donor-acceptor bipolar molecules based on carbazole and quinoline moieties, which behave as acceptor (A) or donor (D) respectively. The synthesized materials CzPPQ and mCzPPQ demonstrate maximum fluorescence intensity at 417 nm and 413 nm in the solid state, and 396 and 402 nm in the toluene solution with fluorescence quantum efficiency of 67%, 8%, respectively. Investigated molecules pCzPQ and mCzPQ showing bipolar nature and form blue excited complexes (464 nm and 458 nm) with 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) acceptor and orange (551 nm and 546 nm) with 4,4′,4′′-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) donor. White organic devices comprised of two interface exciplexes m-MTDATA : mCzPPQ (orange exciplex) and mCzPPQ : PO-T2T(blue exciplex) in the three-layers sandwich-type OLED allowed us to obtain warm-white electroluminescence. Fabricated and optimized white non-doped devices with the structure consisting of m-MTDATA/ orange exciplex/mCzPPQ/blue exciplex/PO-T2T light-emitting system demonstrated white electroluminescence with a high colour rendering index of 76 and colour temperature of 8400 K and maximum external quantum efficiency of 3.15 %.

References:
Diphenylsulfones para-substituted by diverse electron-donating fragments as TADF emitters

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Abstract:

Thermally activated delayed fluorescence (TADF) [1] is shown by organic molecules due to the reverse intersystem crossing from triplet excited to singlet excited states caused by the thermal motion of atoms and the following charge transfer emission [2]. This approach allows to employ triplet excitons by converting them to singlet excitons for luminescence and overcome spin statistical 25% limit of internal quantum efficiency of organic light emitting diodes (OLEDs). Employment of TADF emitters for the fabrication of OLEDs became widespread in recent years due to the possibility of replacing high-cost phosphorescent emitters based on rare metals. In 2012 Adachi et al [3] reported on the first class of deep-blue TADF emitters designed using diphenylsulfone moiety as an acceptor. The advantage of this type of acceptor moiety is in tetrahedral geometry of sulfonyl group which helps to avoid conjugation in the compound thus leading to strong intramolecular charge transfer. In addition, diphenylsulfone moiety has electron-withdrawing properties caused by significant electronegativity of oxygen atoms [4]. We synthesized and characterized a series of new donor-acceptor-donor type diphenylsulfone-based TADF materials and studied them in host-guest systems in order to test the optimized systems in OLEDs. The optical, thermal, electrochemical and photoelectrical properties of the synthesized compounds have been investigated. All the compounds were found to be capable to form glasses with glass transition temperatures ranging from 68 to 162 °C. They exhibited high thermal stabilities, with 5% weight loss temperatures exceeding 433 °C. Ionization potentials of the solid samples were ranged from 5.03 to 5.74 eV. The charge-transporting properties of the synthesized materials were studied by time-of-flight method. Some of the synthesized compounds exhibit ambipolar charge transport properties. These compounds were tested as emissive species for the fabrication of OLEDs.

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References:

Influence of trapping effects on organic memory devices

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Abstract:

Organic memory devices (OMEMs) are realized by integrating a layer of the crosslinkable dithienylethene XDTE in a solution-based multilayer OLED stack. The photochromic XDTE molecule can be switched reversibly by a photo- and/or electrically induced ring-opening/-closing reaction to two thermally stable states featuring different physical properties. [1] The change in the energy level positions, which is responsible for controlling the hole injection by shifting the hole injection barrier, [2] enables a high ON/OFF ratio approaching $10^6$. For future application as data storage element, electrically induced switching is of great importance, but the charge trapping landscape is affected by this switching mechanism. By incremental switching via current densities pulses, intermediate switching states are accessible. [3] The current-response is analysed as a function of the fraction of closed isomer obtained via in-situ reflectance absorption spectra. In combination with impedance spectroscopy measurements, we study the role of trapping effects in this energetically anisotropic switching process.

![Energetic difference of the photo- and electrically induced opening process of XDTE based OMEMs](image)

References:

Fabrication of a nanogap light-emitting electrochemical cell

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Abstract:
Electrically driven single-molecule light-emitting devices are expected to be applied to new single molecular electronics devices and single-photon sources. However, it is generally difficult to fabricate a single molecular junction between fixed electrodes and realize bipolar charge injection from a nanogap electrode which consists of same metals to the molecule. In this study, we propose a nanogap light-emitting electrochemical cell (LEC) [1], that is to be a new single-molecule light-emitting device without using single-molecular junctions. In LECs, due to the motion of the electrolyte mixed in the light-emitting polymer, highly efficient bipolar charge injection and light emission occur regardless of the work function of the electrodes and interelectrodes distance. We fabricated a LEC by using a mixed film of light-emitting polymer (F8BT) and ionic liquid (P66614-TFSA) between nanogap electrodes and observed an electrically driven light-emission.

A gold electrode pattern was drawn on the SiO2 substrate by a conventional electron beam lithography technique, and it was immersed in Octadecyltrichlorosilane (OTS) solution (1 mM, dehydrated cyclohexane solvent) for 24 hours to control the deposition pattern of the organic film. The nanogap electrode was then formed by the electromigration method. F8BT and P66614-TFSA were mixed at a weight ratio of 4 : 1 and spin-coated (3000 rpm) on the substrate. The device characteristics were measured at a room temperature under the atmosphere. Fig. 1 shows the AFM image of the device. The organic film is formed only on the electrodes and nanogap owing to the OTS surface treatment on SiO2. Therefore, the electrically-driven light-emission is expected to occur at the nanogap electrode. Fig.2(a) and 2(b) shows current-time and luminescence intensity-time characteristics of the nanogap LEC, respectively. A constant voltage of 10 V was applied after 20 s. Spike like current and light emission were simultaneously observed, indicating that the current-driven light-emission occurred.

Fig.1 AFM image of the nanogap LEC.

Fig.2 Current-time (a) and photomultiplier tube (PMT) current-time (b) characteristics of the nanogap LEC.

References:
A Comprehensive Study of Structurally Engineered Double-layer Memristors

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Abstract:

The memristor is believed to be the fourth two-terminal fundamental passive element, and a memristor model was successfully developed by Hewlett-Packard scientists in 2008 on the basis of the original theoretical framework of the memristor, which was published by Leon Chua in 1970 [1]. We demonstrate the fabrication of a memristor device based on Al/TiO$_2$/TiO$_x$/Al/TiO$_2$/TiO$_x$/Al double-layer structure. TiO$_2$ thin film was deposited using an atomic layer deposition technique, and the TiO$_x$ thin film was coated on the TiO$_2$ layer with radio frequency magnetic sputter technology. The Al/TiO$_2$/TiO$_x$/Al/TiO$_2$/TiO$_2$/Al double-layer memristors will be able to make nanoscale switching capability to change their resistance state between high and low as a switching device within crossbar arrays and showing a forming-free resistance switching behavior [2]. The crossbar arrays structure is observed to affect the switching mechanism in the memristor device. The research presented here can provide a new memristor structure for exploring the possibility of a high-performance memristor device for electronic applications.

Fig. 1 Schematic representation of TiO$_2$/TiO$_x$ based memristor device.

Fig. 2 Switching I-V curves of the double-layer memristor with 1-2 layer and 2-3layer, respectively.

References:


Control of molecular orientation in diindenoperylene films by underlying few-layer MoS₂ substrate

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Abstract:

Recently developed one-zone sulfurization technique [1] enables fabrication of uniform, large-area few-layer MoS₂ films with a high degree of crystallinity. In this contribution, we show that the crystallographic orientation of MoS₂ c-axis is directly influenced by the layer thickness and/or sulfurization temperature. To be more specific, the c-axis varies from the out-of-plane to in-plane orientation for samples with the MoS₂ thickness of 3 and 9 nm, respectively. Furthermore, we found out that the c-axis orientation subsequently controls the orientation of small organic molecules, such as diindenoperylene (DIP), grown on the top of MoS₂ layer. Employing the grazing-incidence wide-angle X-ray scattering (GIWAXS), we observed that the DIP molecules are oriented in the lying-down configuration when the c-axis is normal to the substrate plane and adopt the standing-up orientation when the c-axis is oriented parallel to the substrate plane, see Figure 1. To the best of our knowledge, the molecular orientation was so far manipulated exclusively by selecting an appropriate substrate [2], but a different molecular orientation on the same kind of substrate was not observed up to now. This result has direct implications for a tailored preparation of small-molecule organic films for diverse applications in (opto)electronics.

![Figure 1](image)

*Figure 1: Reciprocal space map shows 002 diffraction peak, coming from the MoS₂ layer with a thickness of a) 3 nm and b) 9 nm, and 001 reflection of the 13 nm thick layer of DIP.*

References:


Through-space charge-transfer of carbazole-imide derivatives resulting in aggregation enhanced and thermally activated delayed fluorescence.

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Abstract:

All-organic emitters exhibiting thermally activated delayed fluorescence (TADF) have great potential for applications in organic light-emitting diode (OLEDs) since they allow harvesting of both singlets and triplets generated under electrical excitation \cite{1}. Using TADF materials, 100\% transformation of electricity to light can be achieved. High photoluminescence quantum yields (PLQY) and small singlet-triplet energy splittings ($\Delta E_{ST}$) of TADF emitters have to be obtained which are not trivial tasks.

Aiming to maximize PLQY and minimize $\Delta E_{ST}$ of TADF emitters, we designed and synthesized two carbazole-imide derivatives in which chromophores are linked via spacer. Such molecular design can allow to separate electrons and holes on two different donor and acceptor units which results in extremely low $\Delta E_{ST}$ values. It was shown by time dependent density functional theory (TD-DFT) calculations that HOMOs of the compounds are mainly located on the electron-donating carbazole moieties while LUMOs are located on the electron-deficient imide fragments. The molecules were found to be twisted with calculated torsion angle close to 75° in the ground state, which usually leads to small $\Delta E_{ST}$. The results of single crystal X-Ray analysis revealed that torsion angles for one carbazole-imide derivative between carbazole and benzene ring planes was 69° while carbazole plane and benzene ring plane formed angle of 86°. Additionally, N-C interatomic distance was estimated to be 3.227 Å and this distance was found to be less than the sum of the van der Waals radii of C and N (3.25 Å) which usually leads to n→π* interaction between carbon atom of carbonyl group and nitrogen atom of carbazole. For the solid sample PLQY value of 20\% was observed. The emission enhancement can apparently be explained by the restriction of intramolecular rotations without the planarization of the molecular structure. To investigate the nature of charge transfer in the studied molecules, photoluminescence (PL) spectra and PL decays of the derivatives dispersed in ZEONEX matrix were recorded. The obtained results show intramolecular nature of the through-space charge transfer resulting in TADF. TADF properties of the studied molecules were additionally characterized by steady-state and time resolved measurements at different temperatures. Using the developed emitters, The best greenish-blue OLED fabricated using the developed emitters exhibited maximum current, power and external quantum efficiencies of ca. 6.7 cd/m\textsuperscript{2}, 4 lm/W and 2.3 \%, respectively, without out-coupling.

Acknowledgements

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References:

Exciplex-based approach for highly efficient organic light-emitting devices

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Abstract:

Organic exciplex-based systems that display thermally activated delayed fluorescence (TADF) are widely used in highly efficient organic light-emitting diodes (OLEDs) [1]. Since electrons and holes are positioned on two different molecules, in exciplex-based systems small singlet-triplet splitting (ΔE1-3≈0–0.03 eV) can be realized much easier than in single TADF molecules. TADF contribution in exciplex-based OLEDs can be maximized and theoretical internal quantum efficiency of 100% can be achieved [1].

In this presentation, several approaches of application of exciplex-forming systems in high-efficiency oleds exhibiting TADF will be demonstrated. Interface exciplex host, was applied for optimization and enhancement of performance of non-doped OLEDs based on new emitters showing aggregation induced emission enhancement (AIEE) [2]. The color-tunable OLEDs with the minimal number of the functional layers were designed and fabricated [3]. The voltage-dependent green-blue electrofluorescence was obtained due to unique physical properties of the new ambipolar fluorophore 3,6-di(4,4’-dimethoxydiphenylaminyl)-9-(1-naphthyl)carbazole. Electroluminescence spectrum of the devices contained the blue fluorescence band, strong interface exciplex emission band with the emission maximum at ca. 540 nm, and voltage-dependent electroplex emission bands in the region of 550-650 nm [3]. OLEDs based on carbazole and tetrphenylethylene derivatives exhibiting emission from both excitons and exciplexes based on aggregation-induced emission were designed fabricated and charaterized [4]. Extremely efficient warm-white OLEDs with harmless for the human eyes electroluminescence spectra designed [5]. In the designed OLEDs, sky-blue TADF of a carbazole derivative is combined with the yellow-orange exciplex emission of this derivative and a commercial donor material. The best device demonstrated very high brightness of 40900 Cd/m² (at 15 V), current efficiency of 53.8 Cd/A, power efficiency of 19.3 lm/W. E external quantum efficiency of the device reached 18.8 %.

Acknowledgements

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References:

Could we improve the stability and the luminescence of copper (I) diimine complexes by a new chemical design of the phenanthrolines?

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**Abstract:**

Copper(I) complexes CuL$_2^+$ where L is a diimine ligand are low cost and non-toxic species, which are well known for their interesting photo-physical properties. Our main interest concerning these complexes is the luminescence, that is mainly ruled by the steric hindrance at positions 2 and 9 of the phenanthroline (figure 1a). The bulkier the substituent, the more the luminescence quantum yield is notable because non-radiative deactivation pathways are disfavored. We can quote for example [Cu(dsbtmp)$_2$]$^+$ (dsbtmp=2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenantroline)$^{1,2}$ whose high quantum yield, about 6.3% with a lifetime of 2.8 µs were demonstrated by Castellano et al.. However, one of the major issues of these molecules is their stability. In the same way that steric hindrance in positions 2 and 9 of phenanthroline increases luminescence, it also increases the instability of the complexes. Burstyn et al. have demonstrated with Bis(2,9-di-tert-butyl-1,10-phenanthroline)copper(I) complex$^{3,4}$ that really impressive photophysical performances could be reached by using tert-butyl substituents in positions 2 and 9 of phenanthroline, but the former complex proved very unstable because of the huge steric strain imposed by tert-butyl groups.

**Could we improve the stability and the luminescence of copper (I) diimine complexes by a new chemical design of the phenanthrolines?**

In order to solve this problem, we imagine a new chemical engineering for phenanthrolines, namely substituting position 2 by a bulky aliphatic group (to promote luminescence) and position 9 by an aromatic group (to stabilize the coordination sphere). Thus, we designed three new ligands (1), (2) and (4) composed of one aromatic stabilizing group able to do π-staking with vicinal phenanthroline ligands in the copper(I) complex and one bulky ramified alkyl group. We studied the impact of the latter (using both iPr and tBu) as well as the effect of a spacer between phenanthroline and the aromatic ring (CH$_2$ vs. direct bonding). This presentation will focus on the synthesis, photophysical characterizations and stability study of this family of four copper(I) complexes with asymmetric phenanthrolines ligands.

![Figure 1: a) Phenanthrolines numbering b) Family of copper(I) complexes.](image)

**References:**

Carbazole-based hole transporting material for efficient and stable perovskite solar cell

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Abstract:

The organometal halide perovskite solar cell (PSC) is currently widely studied due to its good photovoltaic performance and low cost fabrication technique [1]. However, PSCs still need to overcome several drawbacks like instability of the device performances [2]. The stability of PSCs is influenced by several factors, such as the perovskite materials, moisture, the hole transporting materials (HTMs), … [1]. The HTMs layer impacts the power conversion efficiency of the devices and can act as a perovskite protective layer avoiding diffusion of moisture [2,3]. The literature reference HTM (Spiro-OMeTAD) as well as most of organic HTMs are usually doped with bis(tri-fluoromethyl)sulfonyl) amine lithium salt (Li-TFSI) and 4-tertbutylpyridine (TBP) to enhance the electrical properties of the HTM layer [1]. However, the addition of hygroscopic Li-TFSI decreases the hydrophobicity of HTMs and limit its role as a protective layer [2,4], decreasing the stability of the device. The scientific community tend to solve this problem by synthesizing hydrophobic HTMs [4]. In the present work, we synthesized novel hydrophobic HTMs based on carbazole moiety, which improve the device stability even though they are doped with Li-TFSI and TBP. All the devices were fabricated with FTO/TiOx/ MAPbI3-xClx/HTM/Au electrode configuration. These HTM show improvement of the stability compared with Spiro-OMeTAD reference. Therefore, they can be considered as promising candidates as HTM in perovskite solar cells (PSCs).

![Normalized stability curves of the device efficiencies (η) of novel HTM based on carbazole moiety under AM 1.5 illumination conditions](image)

Figure 1 : Normalized stability curves of the device efficiencies (η) of novel HTM based on carbazole moiety under AM 1.5 illumination conditions

References

Polarized Emission of Mesogenic Conjugate Polymer by Photo-Commanding Layer

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Abstract:

The control of orientational ordering of conjugate polymer has been of interest for improving the performance of light-emitting diodes [1]. Liquid crystalline (LC) conjugate polymers have been widely studied due to their self-orientational ordering, obtained by rubbing method [2]. Although the rubbing method is a promising technique for aligning the LC, this could give rise to performance degradation in the electro-photonic devices since an electrostatic effect and an large surface roughness.

In this work, we demonstrate highly polarized emission of LC conjugate polymer, poly(9,9-di-n-octylfluorenyl-2,7-diyl-alt-(benzo[2,1,3]thia-diazol-4,8-diyl)) (F8BT), via photoalignment method. Here, the photoalignment layer is acted as a hole transport layer and an electron blocking layer in a conventional organic light emitting diode (OLED). Also, the photo-commanding layer is easily governed by controlling the polarization of ultra-violet (UV) light. The surface anchoring energy was measured to be similar to the anchoring energy by the rubbing method. However, the surface roughness was remarkably reduced from 3.1 nm to 0.8 nm (rms). Figure 1 shows the microscopic textures of the F8BT film on the photo-commanding layer under crossed polarizers and the polarized spectra. When the photo-aligning direction was parallel to one of crossed polarizers, an excellent dark state was observed. In addition, a polarization ratio of the photoluminescence (PL) was measured to be similar to that of the rubbed F8BT film. This method would be applicable to the emitting devices with the patterned polarization such as stereoscopic 3D display [3].

Figure 1. Microscopic textures under crossed polarizers and polarized PL spectra parallel and perpendicular to a sample-orienting direction. Letters P, A, and S represent the directions of the polarizer, the analyzer, and the sample orientation (photo-aligning direction), respectively.

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References:

How can non fullerene acceptors help to print stable high efficiency polymer solar cells?

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Abstract:
Non fullerene acceptors (NFAs) have recently attracted high intention due to their strong potential to improve power conversion efficiency (PCE) of organic solar cells (OSCs). Indeed an unprecedented increase in the device performance of OSCs since 2015 could be observed through the arising of new NFAs leading now to PCEs > 13 % in single junction solar cells [1], while even 17.3 % efficiency could be reached in tandem solar cells [2]. As now theirs performances make OSCs as photovoltaic technology highly promising for a large number of niche markets, it is important to study aspects such as processing of OSCs with industrial relevant materials and techniques and even more important stability of the NFA based OSCs. Some first results presented during the last years have shown that OSCs based on NFA held great promise for improve device stability compared to fullerene based acceptors [3]. More recently Brabec and coll. have studied the stability of one of the most representative NFA family, namely ITIC, blended with the PBDB-T donor polymer under light soaking test. It was found that ITIC-Th and ITIC-2F blended with PBDB-T lead to OSCs with lifetime approaching 10 years [4]. However in all those studies, the device structure was composed of partly evaporated layers (hole extraction layer and Ag electrode) and solution processing of the devices was performed under inert atmosphere demanding therefore more details investigation under more industrial relevant material and processing conditions.

In this work, we study two ITIC derivatives in combination with PBDB-T as well as PTB7-Th towards stable fully solution processed high efficiency OSCs. The stability of the NFA based OSCs is compared to device using PTB7-Th:PC71BM blend as highly stable reference material [5] that has recently demonstrated constant high efficiency under light soaking over 10 years. First we demonstrate that replacement of MoOx as HTL by PEDOT:PSS introduce only performance losses from 9.4% for PBDB-T:ITIC to 7.7% making fully printed OSCs possible. As interfacial layers plays important role in the stability of OSCs [6,7], their impact as well as that of the donor polymer and processing conditions on the device stability are investigated under ISOS L-1, ISOS T1 and ISOS D1 using simulated AM1.5 lighting as well as UV @ IR free LED lighting. Finally, the stability of fully inkjet printed ITIC based solar cells is evaluated

References:
Ambipolar organic field-effect transistors based on the dicyanodistyrylbenzene copolymers

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Abstract:

Three types of dicyanodistyrylbenzene (DCS)-based copolymers (PBDT-DCS, PT-DCS, and PNDI-DCS) present ambipolar charge transport characteristics in organic field-effect transistors (OFETs). Because introduction of the DCS moiety in a polymer backbone not only lowers the lowest unoccupied molecular orbital (LUMO) level, but also increases the crystalline ordering via interchain dipole-dipole interactions. As a result, the highest occupied molecular orbital (HOMO) energy levels of polymers were determined to be −5.53, −5.56, and −5.70 eV, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of PBDT-DCS, PT-DCS and PNDI-DCS are estimated to be -3.76, -3.84 and -3.92 eV, respectively. The three polymers showed HOMO and LUMO levels close to -5.5 eV and -4.0 eV, respectively, which can show efficient injection of electrons and holes from the Au electrode to improve ambipolar charge transport. The determined hole/electron mobilities of the OFETs were 0.064/0.014, 0.492/0.181, and 0.420/0.447 cm2/Vs for PBDT-DCS, PT-DCS, and PNDI-DCS, respectively, after thermal annealing at 250 °C. By incorporating the electron-deficient naphthalene diimide (NDI) unit in the copolymers, the n-channel transport was enhanced, with decreasing frontier molecular orbitals with enhanced electron injection from the Au electrode. Therefore, PNDI-DCS provided equivalent hole and electron mobilities with completely symmetric output curves in the positive and negative drain voltage regions. A complementary inverter was successfully fabricated, which benefitting from the balanced ambipolar feature of the PNDI-DCS OFETs.

Output characteristics of the OFETs based on 250 °C-annealed film and voltage transfer characteristics of the complementary inverter based on the PNDI-DCS OFETs.
Growth morphologies and thermalization pathways of nitrogen based oligoacene derivatives on (0001) sapphire

Aydan Çiçek, Aleksandar Matković, Markus Kratzer, Zhongrui Chen, Olivier Siri, Conrad Becker, Christian Teichert

Abstract:

Oligoacenes (as pentacene) and their derivatives are considered as potential candidates in the field of organic electronics due to their molecular packing that favors charge transport and thus high field-effect mobilities. Here, dihydro-tetraaza-pentacene (DHTA5) and dihydro-tetraaza-heptacene (DHTA7) molecules are considered [1,2]. Both molecules exhibit a similar dipolar momentum and hydrogen bonding in the crystal, but have a different size of the backbone. Molecular arrangement, nucleation densities, sizes, and shapes of the resulting crystallites are analyzed as a function of the deposition temperature [3].

The molecules are deposited using a hot wall epitaxy system. As substrate, vicinal (0001) sapphire is used with an average step distance of 50 nm, and step height of 0.2 nm. The morphology of the grown films is investigated ex-situ by atomic force microscopy. Coverages from sub-monolayers to several layers are analyzed, and evolution of needle-like and island-like crystallites is examined as a function of the deposition temperature. An activation energy of (1.23 ± 0.12) eV was found for the nucleation of DHTA7 islands (composed of upright standing molecules), while (1.16 ± 0.25) eV was obtained for DHTA5 needles (composed of lying molecules). The observed disparity in the temperature dependent nucleation densities of the two molecular species is attributed to the different thermalization pathways of the impinging molecules [4].

References:

Ultra-narrow Bandwidth Organic Photodiodes by Exchange Narrowing in Merocyanine H- and J-aggregate Excitonic Systems

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Abstract:
The solid-state packing structure of π-conjugated organic molecules highly affects the materials’ properties.[1] For merocyanine dyes, usually arranging in an H-coupled antiparallel fashion,[2] more interesting J-coupling structures have rarely been reported. Here we show for nine highly dipolar merocyanines with the same π-scaffold and thus equal monomer properties in solution, that the packing arrangement can be controlled by the bulkiness of the donor substituent, leading to strong exciton coupling within a card stack (H) or zig zag (J) packing.[3] Both bands in the blue (H) and NIR (J) spectral ranges arise from a single exciton band and are not just a mere consequence of different polymorphs within the same thin film. By fabrication of organic thin-film transistors, these dyes are demonstrated to exhibit hole transport behavior in spin-coated thin films. Moreover, when used as organic photodiodes in planar heterojunctions with C_{60} fullerene, they show wavelength-selective photocurrents with external quantum efficiencies up to 11 % and ultra-narrow bandwidths down to 30 nm.[4] Thus, narrowing the linewidths of optoelectronic functional materials by exciton coupling provides a powerful approach to yield ultra-narrowband organic photodiodes.

References:
Infrared studies of device relevant layers - energetic and morphological insights

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Abstract:

Organic optoelectronic devices consist of stacked organic and inorganic materials. The device performance is mainly influenced by the interface of these layers. Increasing the interfacial compatibility especially between the transparent conductive oxide electrode and the organic semiconductor layer can improve the charge carrier transport through the stack and thus the efficiency of the device. The investigation of the structure-function relationship of these layers is a major key to the basic understanding of the fundamental mechanisms in organic electronics.

Thin films of metal oxides are known to be excellent charge-selective interlayers in optoelectronic devices. [1,2] In this study, solution-processed nickel oxide as hole transport layer and tin oxide as electron transport layer were investigated by infrared spectroscopy. This method gives insight into the composition of the investigated material and can monitor orientation of characteristic vibrations or functional groups. We studied the influence of annealing temperature on bulk and surface properties of the metal oxide layers. [2] In comparison with photoelectron spectroscopy, atomic force microscopy and device characteristics a better understanding of the energetic, chemical and morphological properties at the interface can be achieved helping to improve device performance.

References:


Naphthothiazine and Acridine spiropyrans for electronic applications

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Abstract:

Molecular electronics requires systems capable of receiving, storing and processing information. Photochromic processes can be considered as “elementary” acts of recording information by actinic light.

\[ 0 \rightarrow 1 \quad A \xrightarrow{h\nu} B \]

In this work, we synthesized and investigated photochromic materials based on spiropyrans, with improved for practical application of spectral-kinetic properties. Their photoinduced form is a merocyanine dye (B).

\[ \text{1-R=H, 2-R=5',6'-benzo, 3-R=8'-OMe, 4-R=7'-NEt}_2 \]

Photochromic properties of spiropyrans of the naphthothiazine (1–4) and acridine series in liquid solutions have been studied. Flash photoexcitation of solutions of 1\textit{A}–4\textit{A} in toluene and ethanol at room temperature induced absorption in visible region, and the absorption pattern did not change to an appreciable extent if air was present in the system. The absorption maximum of the colored form in more polar solvent appeared at longer wavelengths. Unlike indoline and phenanthridine spiropyrans, colored isomers 2\textit{B}–4\textit{B} exhibit positive rather than negative solvatochromism, indicating their predominantly quinoid structure. The absorption maxima of the colored form of unsubstituted derivative (1\textit{B}) in ethanol and toluene are almost similar. On example of the naphthothiazine (1–4) and acridine spiropyrans, the factors contributing to the improvement of light resistance are experimentally illustrated: the absence of a nitro group in the structure of the molecule, the singlet path of photocoloration, a quinoid structure, and a short lifetime of the photoinduced form.

The study was supported by the Russian Ministry of Education and Science (Project 4.4697.2017/6.7), Committee on Science and Higher School of St. Petersburg and Russian Foundation for Basic Research (Project 16-08-01299).
Resonance Raman spectra of molecules exhibiting ultrafast excitation energy transfer

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Abstract:
It has been found that the rate of intramolecular excitation energy transfer in many molecules where the donor and acceptor moieties are connected via a conjugated bridge exceeds by up to several orders of magnitude the rate which would correspond to purely Förster type energy transfer (see e.g. [1]). For this process, the term „through-bond“ energy transfer has been coined. It differs from the „through-space“ Förster energy transfer also by its independence on spectral overlap and mutual orientation of corresponding transition dipole moments. However, the true nature of the „through-bond“ energy transfer remains unclarified. One of the considered contributing mechanisms is superexchange interaction where the molecular orbitals of the bridge are involved in the Dexter-like energy transfer mechanism (see e.g. [2]). Another approach introduced by Okuno [3] considers the energy transfer as a non-adiabatic transition. Recently, Athanasopoulos and coworkers performed excited-state molecular dynamics simulations of a donor-acceptor molecule exhibiting the „through-bond“ energy transfer [4]. Their results show that the molecule undergoes transient delocalization within several femtoseconds after photoexcitation of the donor and then gradually relaxes towards the state with the excitation energy localized on the acceptor moiety. According to Heller’s time-dependent formulation of the Raman scattering, such early dynamics of the excited state should be reflected in resonance Raman intensity pattern of the molecule [5]. Thus, in this contribution we describe our attempt to measure resonance Raman spectra of compounds containing 1-aminopyrene donor(s) and 3-aminobenzanthrone acceptor connected via sym-triazine bridge [6] using 355 nm excitation wavelength. These compounds were shown by transient absorption and transient lens measurements to undergo very efficient excitation energy transfer on timescale shorter than 200 femtoseconds [7].

References:

Acknowledgement: The support by the project No. CZ.02.1.01/0.0/0.0/16_019/0000778 of the Ministry of Education, Youth and Sports of the Czech Republic is gratefully acknowledged.
Pyrene-Based Compounds In Organic Optoelectronic Applications

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Abstract:

Fused, ladder-type organic materials have inherent advantages, such as extended π-frameworks, favorable stacking behavior in the solid state, conductivity, and high field-effect mobility. We report a wide range of extended pyrene-based compounds so called quinoxalinophenanthrophenazine (TQPP), Figure 1. The introduction of nitrogen atoms in the TQPP core decreases the HOMO-LUMO gap making the compounds of more interest in electronic applications. Besides, the planarity of the core in the TQPP compounds facilitates the efficient cofacial stacking of the materials in the solid state and increases the intermolecular π-orbital overlap. Combining the electronic properties of the electron-deficient TQPP chromophore and the predisposition of the TQPP compounds to self-organize into efficient self-assembled π-π columnar stacks in a single molecule offer an interesting combination of physical properties and, perhaps, a route to new materials for electronic applications. In this talk, we will discuss the different properties and features of the TQPP compounds.

Figure 1. Chemical structure of TQPP-[X]2-[Y]4.
Improvement of organic photovoltaic cells performances by the insertion of dipolar SAMs-functionalized metal oxides

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Abstract:

The insertion of very thin metal-oxide (MOx) semi-conducting (SC) layers at the interface between the conductive electrodes (FTO/ITO, Metals) and the active layer (polymer, perovskite) has given an efficient solution to improve the separation and collection of free carriers at electrodes and the performances of organic and hybrid photovoltaic devices. In order to avoid the energy losses, carrier’s recombination and to promote the good structuration of organic active blend P3HT: PCBM, the MOx layers have been functionalized by adequately oriented dipolar self-assembled monolayers (SAMs). By choosing two Y-PP-COOH (Y=OCH₃, F) molecules grafted onto n-type and p-type SC MOx layers and having opposed dipolar moment, we exhibit clearly the dipole effect on the Voc (open circuit potential) via the variation of Work functions of oxide layers. The SAM may also influence the surface energy of MOx layers and so the wetting/organization of the active layer. In these both effects the chemical nature and the orientation of the grafted molecules appear as the key parameters of the solar cells improvements.

Current density versus bias

J (V) for solar cells

FTO/WO₃-SAM/P3HT:

PCBM/ZnO/Al/ under AM1.5 G illumination

----- Without SAMs WO₃

CH3O-PP-COOH

F-PP-COOH
Electronic properties of few layer tungsten oxide WO3 on gold (111) surface modified by tetraphenyl porphyrin and grafted dipolar molecules studied by STM and spectroscopy

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Abstract:

Tungsten oxide WO3 is used in organic and hybrid/inorganic electronics as p-type semiconductor and hole transport layer (HTL). The WO3 which may be inserted between the conductive electrodes (FTO/ITO, Metals) and the active layer (molecule, polymer, perovskite) has given an efficient solution to improve the separation and collection of free carriers at electrodes and the performances of organic and hybrid photovoltaic devices. Our goal is to study the properties of mono or few layers of WO3 as a promising candidate for photoharvesting, electronic interaction with molecules -such as porphyrin and dipolar molecules- and charge transfer processes. WO3 shows tendency to form 1D structures (amorphous), 2D periodic monolayers and 3D islands. I-V spectra reveal diode type behavior for 2D periodic islands and 3D islands whereas 1D structures show metallic I-V characteristic. As example, dl/dV spectra of porphyrin molecule on 1D structures shows an increase in the band gap (~ 0.8 eV).

Figure-1a: STM image showing different structures of WO3 at 10 pA and 1.5 V
Figure-1b: dl/dV spectra for points marked in fig-1a
Figure-2: STM image showing porphyrin molecules on Au and on WO3 10 pA and 1.5
Modulating Fluorescence with Supramolecular Contacts

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Abstract:

Although azomethines have the benefit of being easily prepared, their properties can be limited. This is the case for their photoemission where their quantum yields are limited. In fact, the imine bond undergoes both photoisomerization and photoinduced electron transfer. These deactivation pathways can efficiently quench the fluorescence of otherwise intrinsic fluorescence fluorophores. Therefore, azomethine incorporation in conjugated organic fluorophores leads to substantial fluorescence quenching. These deactivation modes can be mitigated by intermolecular contacts, especially in terms of aggregation induced emission. A red colored conjugated azomethine was prepared having urea end-groups. These were to promote hydrogen mediated emission enhancement by intermolecular hydrogen bonding. It will be demonstrated that emission enhancement is possible both in protic solvents and when aggregated. It will be demonstrated that the prepared compound is further electroactive, undergoing electrochemically mediated color changes.

\textbf{X-ray crystal structure of the conjugated azomethine showing the intermolecular hydrogen bonding and supramolecular network, in part responsible for the emission enhancement.}

References:


Towards An Electrofluorescent Switch

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Abstract:
Visible conjugated organic fluorophores have found uses in many applications, including organic electronics, probes, and sensors among many others.1 Pushing the emission envelop into the NIR region has many advantages for both organic electronics2 applications and biological imaging.3 Extending the emission to the NIR can in part be done by incorporating complementary strong electron donors and acceptors into the fluorophore. While -NO2 and -NR2 substituents are typically used as complementary electronic donor-acceptor groups, respectively, the nitro group can lead to undesired limitations such as quenched fluorescence, solvent interactions, and instability. We therefore explored –CN as an alternative functionality for electronic push-pull fluorophores. Electroactivity can additionally be incorporated into the fluorophore when the –NR2 substituent is triphenylamine. The oxidized intermediate of the triphenylamine that can be produced electrochemically can quench the intrinsic fluorophore emission. This leads to an electrochemically mediated fluorescence switch. The photophysical and electrochemical properties of the electrofluorescent switch will be presented, including the spectrotelectrochemical and spectrotelectrofluorescent properties of the fluorescence switch.

References:
(1) He, Z.; Ke, C.; Tang, B. Z. ACS Omega, 2018, 3, 3267.
Photoimmobilization of Electrochromic Layers

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Abstract:
Conjugated azomethines have garnered much attention owing to their ease of preparation. They are also advantageous for property modification that is possible by the judicious choice of their arylamines and aldehydes used in their preparation. While small molecules of azomethines are beneficial for accurate structure-property studies, their high solubility in common organic solvents is problematic. This is particularly the case when using them in electrochromic applications. In such devices that undergo reversible color change with applied potential, the low molecular weight azomethines cannot sustain repeated oxidation/neutralization cycles. This limits the device performance and ultimately results in device failure. Although performant electrochromic devices are possible with azomethine polymers, it is challenging to selectively pattern the electrode surface of the device. We therefore explored the immobilization of low molecular weight azomethines by photochemical means. In fact, standard photolithography could be used to selectively immobilize an electroactive azomethine on the electrode. It will be shown that the immobilization of the layer could be successfully done photochemically. Also, it will be illustrated that the layer was electrochromic and that it was capable of resisting upwards of 80 min of switching.

Top: electrochromism of a triphenylamine azomethine immobilized on an ITO electrode, monitored at 700 nm with applied potentials between 100 and 1100 mV in acetonitrile for given switching times. Middle: colors of the immobilized film in the neutral (left) and (right) states with electrochemical switching. Bottom: cyclic voltammogram of the immobilized film at 100 mV/sec.

References:
Unravelling the Structural Requirements of Conjugated Azomethines for Electrochromics

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Abstract:

Azomethines have been successfully used as functional materials in a wide range of applications such as organic light-emitting diodes,\textsuperscript{1} organic photovoltaics,\textsuperscript{2} memory devices,\textsuperscript{3} and pH sensors.\textsuperscript{4} Their versatility is in part owing to the properties that can be tailored through the selection of aryl aldehydes and amines used for their preparation. Despite this, knowledge regarding the effect of structural effects on the electrochemical and optical properties remains under explored. This knowledge would be beneficial for designing and preparing conjugated azomethines having targeted colors along with reversible oxidation. These are key properties for use in electrochromics, being the reversible color switching with applied potential. Within this context, extensive structure-property studies of the conjugated azomethine (see Figure) were undertaken. This was to understand the key structural requirements for achieving reversible color changes with applied potential and reversible oxidation. The effect of structure of these key electrochemical and spectroscopic properties will be presented.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

\textit{Cyclic voltammograms illustrating the variation in oxidation potential contingent on azomethine structure, while maintaining reversible oxidation.}

References:

Organic push-pull compounds for the sensitization of p-type oxides.
Inverted Grätzel Solar cell and Photocathode for hydrogen evolution

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Abstract:

With theoretical PCE reaching 40%, Tandem Dye Sensitized Solar Cells (T-DSSCs), which are composed of two dye-sensitized photoelectrodes, a photocathode and a photoanode, sandwiching a redox electrolyte, could represent a cost-effective and promising alternative to silicon based solar cells.[1] This poster will report different works done for the development of p-type electrode:
- The synthesis of p-type mesoporous NiO films through ink-jet printing of a sol-gel ink. Multilayer NiO films were formed and different morphologies could be obtained by playing on the interlayer thermal treatment. The different morphologies and thicknesses of the NiO films were correlated to their performance in a p-DSSC configuration. [2]
- The design, synthesis and physical property characterization of four new triphenylamine–bithiophene push–pull dyes with acceptors of increasing electronic affinity, in order to shift their absorption to the red region of the visible spectrum. The dyes were tested in a p-type DSSC configuration with 850 nm NiO ink-jet printed photocathodes and their performances were compared with that of the reference dye P1. [3]
- Time-resolved fluorescence study of a triphenylamine–bithiophene–naphthalimide dye in four solvents of varying polarity using fluorescence upconversion. After photoexcitation, the directly populated state (S1/FC) evolves toward a relaxed charge transfer state (S1/CT). This S1/CT state is characterized by a lower radiative transition moment and a higher nonradiative quenching. The fast dynamic shift of the fluorescence band is well described by solvation dynamics in polar solvents, but less so in nonpolar solvents, hinting that the excited-state relaxation process occurs on a free energy surface whose topology is strongly governed by the solvent polarity. This study underlines the influence of the environment on the intramolecular charge transfer (ICT) process, and the necessity to analyze time-resolved data in detail when solvation and ICT occur simultaneously. [4]
- The molecular assembly of a push–pull organic dye and a cobalt diimine–dioxime catalyst co-grafted on a p-type NiO electrode substrate realized at the CEA Grenoble (V. Artero’s Team). (Photo)electrochemical measurements allowed characterization of electron transfer processes within such an assembly and to demonstrate for the first time that a CoI species is formed as the entry into the light-driven H2 evolution mechanism of a dye-sensitized photocathode. [5]

References:

Seebeck coefficient of AuGe thin films for thermoelectric applications in organic nanoscale devices

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We experimentally study the thermoelectric properties of Au$_x$Ge$_{1-x}$ thin film alloys close to the metal-insulator transition with the goal of obtaining an element with good thermal sensor properties for integration into nanoscale organic devices.

Based on finite element simulations and by taking into account all spurious thermoelectric effects, we have revealed a Seebeck coefficient of the thin film very close to that of Au thin films. Simultaneously we have observed good electrical properties of the thin film allowing its use as a high-resolution thermometer.

As a proof of principle, we have demonstrated the possibility to integrate such an element as the top electrode of a large-area vertical molecular junction, embedding thin (5-15 nm) molecular layers and producing devices in which the AuGe film simultaneously fulfills the functions of a local heater and thermometer.

![Figure 1: a) SEM image of a device intended to measure the Seebeck coefficient of an AuGe thin film alloy. b) Simulated three-dimensional plot of the temperature in said sample for an applied voltage $V_{ab}$ of 2V between the a and b contacts at a temperature $T=150K$ of the environment.](image-url)
Combined SECM and fluorescence microscopy using a water-soluble electrofluorochromic dye as the redox mediator

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Abstract:
The combination of electrochemical and fluorescence techniques has been the subject of a growing interest from the beginning of the 1990s, moving gradually towards more advanced configurations allowing spatio-temporal resolved measurements. However, examples where fluorescence microscopy and SECM are combined are scarce in the literature [1-3]. We recently reported the use of an electrofluorochromic probe both as redox mediator and fluorophore in a combined SECM-fluorescence microscopy experiment [4]. The SECM tip was polarized in order to convert the fluorophore into a non-emissive form and thus switch off luminescence locally and reversibly. The resulting fluorescence intensity modulation was studied by fluorescence imaging and emission spectroscopy. Our first study was however restricted to organic media. We got interested in extending the concept to a water-soluble electrofluorochromic redox mediator, resorufin, under conditions compatible with biological experiments [5]. The tip potential, the tip-substrate distance, the substrate nature and potential (for a conducting substrate) are the parameters that are likely to control the modulation amplitude. Their influence in the positive and negative feedback as well as generation-collection SECM configurations is investigated in detail.

References:
Long distance electron transfer
between redox partner proteins through the aqueous solution

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Abstract:

Despite the importance of electron transfer (ET) between redox proteins in photosynthesis and respiration, the inter-protein ET rate between redox partner proteins has never been measured as a function of their separation in aqueous solution. Here we use electrochemical tunneling spectroscopy (ECTS) to show that the current between two protein partners decays along more than 10 nm in the solution. Molecular dynamics simulations reveal a reduced ionic density and extended electric field in the volume confined between the proteins. The distance decay factor and the calculated local barrier for ET are regulated by the electrochemical potential applied to the proteins. Redox partners could use electrochemically gated, long distance ET through the solution to conciliate high ET specificity with weak binding, thus keeping high turnover rates in the crowded environment of cells.
Electrical properties by CAFM of photo-switchable SAMs grafted on ferromagnetic substrates

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Molecular spintronics aims at developing nanoscale devices with improved performances or new functionalities by using molecules to conduct spin-polarized carriers. A promising approach is to graft these molecules by a self-assembling process to form SAM on a ferromagnetic electrode (FM). Until now, only molecules acting as a tunnel barrier have been studied [1]. Here we use functional molecules (photochromic) whose the conformation and the electrical conductance can change, reversibly, under light stimuli. Based on theoretical work [2], this study has the objective to investigate the relationship between spin-polarized carriers transport and molecular conformations.

Two systems are considered: (i) diarylethene derivative (DDA) SAM (Fig 1A) grafted on lanthanum strontium manganite (LSMO) surface, and (ii) azobenzene derivative (AzBT) SAM (Fig 1B) on cobalt surface. These systems are electrically characterized by CAFM at ambient temperature for the both configurations, in air for LSMO system and under ultra-high vacuum for Co system to avoid the oxidation.

These analyses show a variation of the electrical resistance of the LSMO surface without SAM up to 1200 (Fig. 1C) due to a stoichiometry modification caused by the tip pressure and electrical field [3;4]. For the naked cobalt a similar behavior was observed with a ratio ~ 933 (Fig. 1D) attributed to the oxidation of Co. These effects are strongly reduced with the SAM covering the FM electrode (Figs. 1C-D). However, these features impede the detection of the open/closed weak conductance change of ~5 for DDA, while a clear cis/trans conductance change of about 20 is observed for the AzBT/Co junctions (Fig 1E).

Figure 1: Molecule of DDA (A) and AzBT (B), (C) Image of currents of the naked LSMO showing the lower conductance in the center (dark area) induced by a previous scan (1x1 μm², F=30 nN, ΔV=0.1V, I from 1pA to 1nA) and with DDA SAM (1x1 μm², F=30 nN, ΔV=0.3V, I from 1pA to 1nA); (D) Idem without SAM on Co (1.5x1.5 μm², F=20 nN, ΔV=0.2V, I from 1nA to 10μA) and with AzBT SAM (1.5x1.5 μm², F=20 nN, ΔV=0.1V, I from 100pA to 100nA), (E) 2d Current-voltage histograms for the AzBT/Co junctions (pristine, cis and trans states).

Acknowledgements. We thank P. Seneor and R. Mattana (UMPhy CNRS/Thales) for supplying the LSMO, and the financial support from ANR "spinfun" project.

References:
Study of the adsorption mechanisms of oriented dipoles of carborane-thiol molecules on a flat gold surface

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Abstract:

The surface work-function (WF) of a (semi-)conductor is the key parameter which determines the amount of electrons that can be emitted from its surface and thus it defines the electronic parameters of the electrical junctions which, in turn, define the final characteristics of various electronic devices. One of the possible ways to tune the noble metal WF is the use of Self-Assembled Monolayers (SAMs) of oriented dipoles [1]. However, the applicability of SAMs is limited by relatively low thermal stabilities of organic molecules. In this regard, SAMs of carboranes with exceptionally high thermal stability represent promising candidates and it was shown that silver work-function can be tuned very precisely over a range of 1 eV by using a mixture of oppositely oriented carborane-thiol dipoles [2].

In this work we show the formation of SAMs of carborane-thiols molecules (1,2-(HS)2-1,2-C2B10H10 and 9,12-(HS)2-1,2-C2B10H10) on the smooth gold surfaces of well-defined gold single-crystals [3] using ambient conditions AFM. The detailed comparison of high-resolution topography maps obtained under different deposition conditions will be presented and their physisorption and chemisorption will be discussed.

References:


Molecular Isomerization and self- assemblies from Ditopic Molecules with variable central bridges

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Abstract:
Series of molecules with a format of Bpy-X-Bpy (Bpy is presenting Bipyridine) are synthesized and are investigated by Scanning Tunneling Microscopy (STM) at the solid liquid interface. The bipyridine moiety is employed as molecular terminal groups due to its active capabilities to form selective hydrogen bonds. The central X bridges can vary so as to involve different molecular functionalities. Molecules Bpy-F-Bpy (F is presenting a fluorescein center) are observed to form variable two dimensional (2D) supramolecular networks. Highly ordered gear chains organizations are observed at the none-acid/HOPG interface where Bpy-F-Bpy molecule shows a cis-like conformation. The organizations are stabilized with intermolecular CH-N hydrogen bonds. When involving acid solvents, the surface organizations turn into a 2D linear stripe organization with the Bpy-F-Bpy molecule in trans-like conformation. The intermolecular interaction has been modified to stronger NH-N hydrogen bonds simultaneously. The H⁺ protonation induced Bpy-F-Bpy cis-to-trans isomerization is therefore a multi-scale switch which involves a change from weak to strong hydrogen bonds, and a structural phase transformation of gear chains into a stripe-like organization.

Molecules Bpy-PE2P-Bpy (where PE2P is presenting a biEDOT center) can self-assemble into various ordered organizations on surfaces. The molecule shows a same cis-to-trans isomerization behavior from the bipyridine protonation, whereas the biEDOT central bridge is always locked in its trans conformation thanks to the intramolecular sulfur–oxygen interactions. The cis-bpy-PE2P-bpy conformers form linear supramolecular stripe and herringbone structures. The trans-bpy-PE2P-bpy conformers form both a zigzag structure and supramolecular wires of variable width. In the various supramolecular organizations, the intermolecular hydrogen bonds between the bipyridine units vary, whereas the biEDOT moieties are always aligned with the same organization and the intermolecular biEDOT interactions remain identical as a dominating force for the supramolecular self-assembly.

The cis to-trans isomerization in the supramolecular network of bpy-F-bpy molecules

References:
Double functional switching from photochromic molecules on surface

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Abstract:
Molecules can be switched between different states by different stimuli, including heating, light, and pH. Among these molecules, aromatic azobenzenes are excellent candidates as photochromic molecular switches since they can exist in two forms, the AZO-cis and the AZO-trans isomers [1]. We introduce here two different molecules incorporating an azobenzene group as a central photochromic unit bridging two different terminal groups: bipyridine for the first [Bipy-Azo-Bipy] and terpyridine for the second [Tpy-Azo-Tpy]. The organizations of these molecules on a surface have been investigated by Scanning Tunneling Microscopy (STM). Both molecule self-assemble on surfaces and various supramolecular networks can be observed with a sub-molecular resolution, thanks to the intermolecular interactions of the terminals moieties.

Hence, we studied by STM the different phase transitions induced by the protonation of the bipyridine terminal moieties or by the photo-switching of the photochromic central bridge. Indeed, a multiscale irreversible phase transition upon protonation was already observed on similar molecules consisting of a central bifluorene bridge and bipyridine terminal groups [Bipy-Fl-Bipy] [2]. Using [Bipy-Azo-Bipy], a similar, protonation induced, phase transition involving the switching from a cis-like to a trans like isomers is also observed as depicted in Figure 1. Next we studied the effect of irradiation on the system. The photoswitching transition from the Azo-trans bridge (the stable state) to the Azo-cis can be triggered by UV light and reversed back to its initial state by visible light [3]. The photo-effect on the central photochromes was firstly confirmed in solution by UV-visible absorption spectroscopy and the organisation of the the Azo-cis isomers on surfaces will be presented.

References: