POSTER C1

Self-organization of pentacene grown on Cu(119): electronic states of aligned molecules for monolayer and thicker films.

E. Annese[1], C.E. Viol[2], J.Fujii[2], I.Vobornik[2], G. Rossi[1,2], C. Baldacchini[3], M.G. Betti[3]

[1]Università di Modena e Reggio Emilia, via Campi 213/A, I-41100 Modena, Italy
[2]CNR-TASC LABORATORY, Area Science Park- BASOVIZZA, SS 14, km 163.5, I-34012 Trieste, Italy
[3]Department of Physics, University La Sapienza, Piazzale Aldo Moro 2, I-00185 Roma, Italy

The self organization of pentacene to form ordered film structures can be driven by the large structural anisotropy of suitable metal substrates [1]. We have prepared and studied pentacene films as grown on Cu(119) (Cu(100) vicinal surface with terrace width ~1,15 nm) with a surface science approach, i.e by LEED, STM, STS and ARPES measurements with polarized synchrotron radiation. These films show a long-range ordered structure, with the long molecular axis aligned along the step direction of the substrate.

The formation of a single layer of pentacene molecules on the substrate kept at 373 K, results in long-range-ordered chain structures, as observed in STM images and in the 3 x 7 reconstruction observed by LEED. The character of the interface and molecular states was investigated by measuring ARPES in different experimental geometries, e.g. using linearly polarized synchrotron radiation oriented parallel or perpendicular to the steps of the vicinal surface (i.e. parallel or perpendicular to the longer molecular axis).

As the thickness of the film increases, the intermolecular forces start to play a more important role than interface interaction in determining the relative orientation of the molecules and the electronic properties of the film. In a pentacene multilayer ~2nm thick the orientation of the molecules was observed by STM, which shows still an ordered array of the molecules lying almost flat on the surface. The extent of the intermolecular interaction was evaluated from the ARUPS measurements by looking at the energy dispersion of HOMO band along the molecular plane normal.

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POSTER C2

Interaction of a Zn-porphyrin monolayer with metallic and semiconducting substrates

C. Castellarin-Cudia, P. Vilmercati, G. Zampieri, L. Petaccia, S. Lizzit, A. Goldoni
Sincrotrone Trieste, s.s. 14 Km 163,5 in Area Science Park, 34012 – Trieste, Italy

C. Cepek, A. Verdini, A. Cossaro, L. Floreano, A. Morgante
Lab. Nazionale TASC-INFM, s.s. 14 Km 163,5 in Area Science Park, 34012 – Trieste, Italy

R. Larciprete
CNR-Istituto dei Sistemi Complessi, Via Salaria Km 29.3, 00016 - Rome, Italy

L. Sangaletti, S. Pagliara
Universita` Cattolica del Sacro Cuore, Via dei Musei 41, 25121 - Brescia, Italy

C. Battocchio
Chemistry Dept., University “La Sapienza”, P.le Aldo Moro 5, 00185 - Rome, Italy

G. Polzonetti
Physics Dept., University "Roma Tre", Via della Vasca Navale 84, 00146 - Rome, Italy

Porphyrins are naturally occurring pigments that can be employed as electron donors and sensitizers in artificial photoactive systems, like solar cells [1, 2]. When organic monolayers are used to sensitize and harvest the photo-response of semiconductors, key issues to be addressed are the energy alignments of the molecular orbitals with the semiconductor valence and conduction bands and the timescale of the charge separation and transfer at the interface. Both issues are influenced by the molecular bonding geometry. Also the interaction between organic monolayers and metals is important because the light reflecting back contacts in solar cells are made of Ag, Au or Pt.

In this light we have investigated the interaction of Zn-tetra-phenyl-porphyrin (ZnTPP) molecules with Si(111), TiO_2(110) and Ag(110). These systems were obtained by depositing exactly one monolayer of ZnTPP on the clean substrates in ultra-high-vacuum conditions.

The interaction with the substrates strongly modifies the ZnTPP electronic states because of bonds formation and charge redistribution. NEXAFS spectroscopy indicates that on all these substrates the ZnTPP molecules chemisorb in a flat geometry (i.e. with the macrocycle parallel to the surface plane). Resonant photoemission, which probes the delocalization (charge transfer) of an excited electron in the empty states on the time scale of the core-hole lifetime [3], indicates a very fast (< 5 fs) injection of the ZnTPP excited charge into the substrate bands.

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POSTER C3

Surface electronic states induced by self-organized C on Fe(100)

J. Fujii (1), G. Panaccione (1), I. Vobrnik (1), G. Rossi (1, 2)

(1)TASC-INFM-CNR, Trieste, Italy
(2)University of Modena and Reggio Emilia, Modena, Italy

Bulk carbon impurities segregate at the Fe(100) surface and, upon thermal annealing, can form metastable surface phases with local and long range order and peculiar electronic properties. We present a surface science study of C- segregated Fe(100) with STM, STS, synchrotron radiation angle-resolved photoelectron spectroscopy (ARPES) of the surface structure and electron states.

In particular the $c(3\sqrt{2} \times \sqrt{2})$ structure, observed with LEED for 0.67 atomic layers of C segregated at the iron surface, is found with STM to be due to self-organized carbon stripes made of zig-zag chains along <11> direction on the surface. ARPES data for the $c(3\sqrt{2} \times \sqrt{2})$ C/Fe(100) surface gave evidence of large perturbation of the iron derived states. The surface states observed for clean Fe(100) disappear and new dispersionless as well as dispersive peaks appear in the C modified surface that are consequent of Fe-C hybridization.

POSTER C4

An UHV STM and STS study of self assembled porphyrin/fullerene dyads on Au(111)

F.Matino[1], V.Arima[1], G.Maruccio[1], R.J.Phaneuf[1,2], R.Del Sole[3], G.Mele[3], G. Vasapollo[3], R.Cingolani[1], R.Rinaldi[1]
(1)National Nanotechnology Laboratory (CNR-INFM)- Distretto Tecnologico ISUFI – Università degli studi di Lecce - via Arnesano, 73100 Lecce (ITALY)
(2)Department of Materials Science and Engineering, University of Maryland and Laboratory for Physical Science, College Park, Maryland 20740
(3)Dipartimento di Ingegneria dell'Innovazione - Universita' degli Studi di Lecce- via Arnesano, 73100 Lecce (ITALY)

Photosynthesic capability, i.e. light conversion into energy is by far the most important characteristic of metallo-porphyrins in living system [1]. In particular, metallo-porphyrins act as chromophores and electron donors in a number of important biological electron-transfer systems including the primary photochemical reactions of chlorophylls in the photosynthetic reaction centers [1]. It has previously been demonstrated that this function is preserved when porphyrins are combined with fullerenes [2] in dyads, acting as donor/acceptor pairs, able to generate photocurrent with important applications in the field of photovoltaic cells. Motivated by this, a number of recent studies [2, 3] have been carried out in order to prepare stable metallo-porphyrin/fullerene monolayers in which metallo-porphyrins and fullerenes are assembled in dyads on surfaces.

In our own work we produce a self assembled monolayer (SAM) of donor-acceptor conjugate dyads on gold, anchoring fulleropyrrolidines onto a metallo-porphyrin SAM. Specifically, we prepare a 4-aminothiophenol (4-ATP) SAM on a gold film, onto which a *meso*-Tetraphenylporphyrins cobalt(II) (CoTPPs) is axially coordinated. Next we deposit fulleropyrrolidines functionalized by pyridil groups (PyC2C60) onto the CoTPPs, interacting with them by axial ligation. The efficiency of these self-assembled donor-acceptor conjugate systems has been already demonstrated in solution [2c].

In this talk we report on different preparation methods of PyC2C60 layers and their characterization by Ultra High Vacuum Scanning Tunneling Microscopy (UHV STM) and Scanning Tunneling Spectroscopy (STS). In creating our samples we have employed both incubation and dipping of a CoTPP SAM in a fulleropyrrolidine solution. The molecular coverage can be tuned by changing the concentration of the solution, the incubation time and the washing procedure. An important step in these procedures is post deposition annealing in UHV environment, which improves the homogeneity of the molecular coverage and reduces the occurrence of fullerenes' aggregates. Optimum annealing results in isolated protrusions whose apparent heights in STM are smaller than those estimated for fullerenes evaporated on gold [4] and which show a bias voltage dependence. These structures appear less bright at negative voltages than at positive ones. This phenomenon is also confirmed in the I(V) curves acquired on single dyads whose asymmetry grade increases by increasing the bias voltage. Our results, including both the STM voltage-dependent images and the highly asymmetric STS curves, reveal the strong interaction between the two moieties of the dyads. An important secondary result of these investigations is a simple and inexpensive method to produce stable monolayers of donor/acceptor dyads, which could be biomimetic to the natural photoenergy conversion systems with applications in photovoltaics.

Acknowledgements: This work was supported by the CNR-INFM, and in part by a NSF US-Italy Cooperative Research Program, #OISE-0242579.

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POSTER C5

Zn-porphyrine/C_{70} complexes: Molecular orientations and electronic properties

P. Vilmercati (1), C. Castellarin-Cudia (1), G. Zampieri (1), L. Petaccia (1), S. Lizzit (1), A. Goldoni (1),
C. Cepek (2), A. Verdini (2), A. Cossaro (2), L. Floreano (2), A. Morgante (2), R. Larciprete (3),
L. Sangaletti (4), S. Pagliara (4), C. Battocchio (5) and G. Polzonetti (6)

(1) Sincrotrone Trieste, s.s. 14 Km 163,5 in Area Science Park, 34012 – Trieste, Italy

(2) Lab. Nazionale TASC-INFM, s.s. 14 Km 163,5 in Area Science Park, 34012 – Trieste, Italy

(3) CNR-Istituto dei Sistemi Complessi, Via Salaria Km 29.3, 00016 - Rome, Itay

(4) Universita` Cattolica del Sacro Cuore, Via dei Musei 41, 25121 - Brescia, Italy

(5) Chemistry Dept., University “La Sapienza”, P.le Aldo Moro 5, 00185 - Rome, Italy

(6) Physics Dept., University "Roma Tre", Via della Vasca Navale 84, 00146 - Rome, Italy

The ultrafast timescale of charge-transfer processes has a crucial relevance in many biological systems and technological devices, involving research fields like femtochemistry, photochemistry, surface reaction dynamics, molecular electronics and solar energy/photosynthesis [1]. Porphyrins are among the most frequently employed building blocks as electron donors and sensitizers in artificial photosynthetic models [2]. It has been envisaged that functionalization of porphyrins with fullerenes can lead to the development of advanced materials with new opto-electronic properties [3]. In this contribution, we demonstrate the feasibility of ultra-high-vacuum self-assembling of porphyrins and pristine C_{70} fullerene molecules on clean substrates with the purpose of fabricating large (cm^2) layered structures having selected intermolecular interactions and electronic properties and to create new bio-mimetic systems appealing as model compounds. Using x-ray absorption, photoemission and resonant photoemission spectroscopy we have investigated the growth, molecular orientation and electronic properties of Zn-Tetraphenyl-porphyrine (ZnTPP) – C_{70} films deposited on Ag(110) and Si(111). These systems can be grown by depositing, molecular layer-by-molecular layer, sandwiches formed by alternate single layers of ZnTPP and C_{70} or by co-depositing the constituent molecules. The quite strong porphyrin-fullerene interaction allows the growth of a single fullerene layer on top of a layer of porphyrin molecules (and *vice versa*), as well as it allows the self-assembling of the two kinds of molecules in an ordered structure when these molecules are co-deposited. Both the interaction with the substrate and the interaction with C_{70} strongly modify the ZnTPP electronic states because of bonds formation and charge redistribution. Resonant photoemission, which probes the delocalization (charge transfer) of an excited electron in the empty states on the time scale of the core-hole lifetime [7] (< 5 fs in our case), indicates that the (ZnTPP) – C_{70} mixed systems delocalize more efficiently the excited electrons as compared to pure ZnTPP films.

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POSTER C6

Surface charges photogeneration in all-thiophene photovoltaic blends: a Kelvin Probe Force Microscopy investigation

Vincenzo Palermo (1) Giovanni Ridolfi (1) Anna Maria Talarico (1) Laura Favaretto (1)
Giovanna Barbarella (1) Nadia Camaioni (1) Paolo Samorì (1,2)

(1) Istituto per la Sintesi Organica e la Fotoreattività - Consiglio Nazionale delle Ricerche, Via Gobetti 101, 40129 Bologna, Italy.
(2) Institut de Science et d'Ingénierie Supramoléculaires (I.S.I.S.) Université Louis Pasteur, 8 allée Gaspard Monge, F-67083 Strasbourg, France

We studied the light-induced generation of charges into an electron acceptor-donor nanoscale phase segregated blend. Two-dimensional maps of the surface potential, with nanoscale resolution in real time, were obtained with Kelvin Probe Force Microscopy [1]. The blend is composed of highly ordered nanoscopic crystals of a modified quinquethiophene, embedded into a regioregular poly(3-hexylthiophene) amorphous grainy matrix, acting as acceptor and donor materials, respectively. Under illumination a change in the surface potential is observed, the acceptor nanocrystals capture the generated electrons, while the donor matrix captures the holes. The presence of particular positively charged crystalline defects was also observed within the film. The charging and discharging of both materials is studied in real time, by also focusing on the influence of different acceptor-donor ratios. Upon a prolonged thermal annealing at high temperatures the chemical structure of the blend was altered, leading to the disappearance of charge separation upon light irradiation [2]. The obtained results are of great importance to improve the understanding of the correlation between the nanoscopic structure of a photoactive material and solar cells performance.

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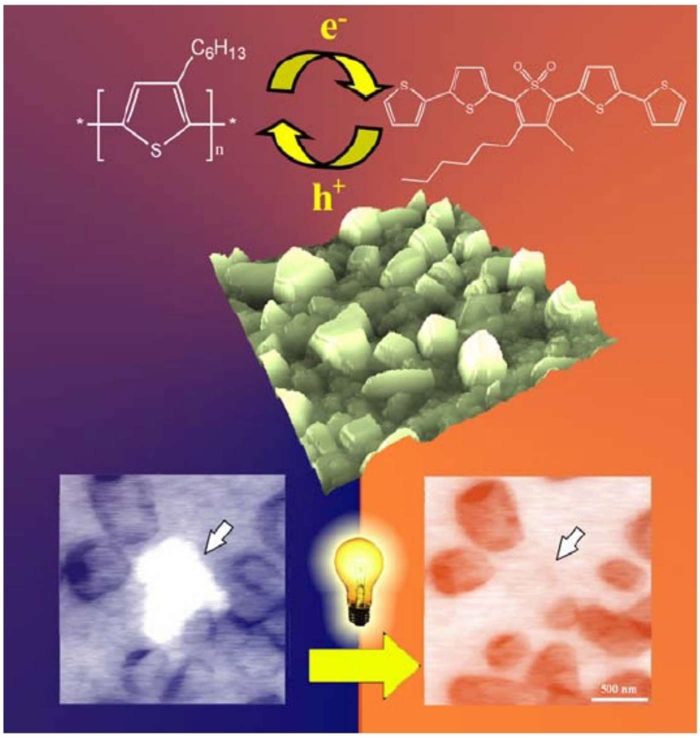

POSTER C7

Photoemission spectromicroscopy investigation of the mechanism of dark-spot degradation of organic light-emitting devices

Luca Gregoratti [a], Sandra Gradonio [a], P. Melpignano,[b] A. Baron-Toaldo,[b] V.Biondo,[b] S.Priante,[b] R.Zamboni,[c] M.Murgia,[c] S.Caria,[c] A. Barinov,[a] M. Kiskinova [a]

[a] *Sincrotrone Trieste ScPA, Area Science Park, SS14-Km163.5, 34012 Basovizza-Trieste, Italy.*
[b] *Centro Ricerche Plast-Optica,Via Jacopo Linussio, 1,33020 Amaro (UD), Italy.*
[c] *Istituto per lo Studio dei Materiali Nanostrutturati del CNR, via P. Gobetti 101, 40129 Bologna, Italy.*

With respect to the other photoelectron microscopy techniques a Scanning PhotoEmission Microscope (SPEM) uses the most direct approach to photoelectron spectromicroscopy which is the use of a small focused photon probe to illuminate the surface. The SPEM at the Elettra synchrotron light souce can operate in two modes: imaging and spectroscopy. In the first mode the sample surface is mapped by synchronized-scanning the sample with respect to the focused photon beam and collecting photoelectrons with a selected kinetic energy. The second mode is photoelectron spectroscopy from a microspot. The SPEM on the ESCAmicroscopy beamline at Elettra has a lateral resolution of 150 nm; and an overall energy resolution which is now better than 200 meV. Utilization of Organic Light Emitting Devices (OLEDs) as low-cost and high efficiency flat displays and illuminators has attracted the interest of optoelectronics industries in the last decade. A major obstacle for vast commercialisation is their relatively short lifetime. This synchrotron study focuses the investigation on one of the most evident failures of an organic LED, the formation of dark spots. The OLEDs were operated in air or in UHV with voltages up to 32 V, in order to provoke faster degradation. The changes in morphology of the initially smooth Al cathode surface during operation evidence a creation of ‘domelike’ structures, followed by local disruption of the Al cathode, exposing micro-areas of the ITO anode and the organic layer. The images taken at the energies of the different chemical species and micro-spot spectra identify a release of volatile In-, Sn- and C-containing species, including metallic In, clear evidence that the degradation is driven by local decomposition of the anode/organic interface.

POSTER C8

Dissipative QCM Monitoring and UV-VIS-NIR Spectroscopy Investigation of Complex Formation at the Surface of Self-Assembled Films

F. Gambinossi, P. Baglioni and G. Caminati

Department of Chemistry - University of Florence - Via della Lastruccia, 3 – 50019 Sesto Fiorentino,
Florence – ITALY

We designed and built functional nanomaterials exposing reactive surfaces, in particular we focused on the process of surface complexation of heavy metal ions.

The nanodevice was produced by direct self-assembly of long chain molecules bearing at one end a complexing moiety for metal ions: we used nitrilotriacetic derivative as complexing agent for nickel ions. The ligand molecule was immobilized as a Self-Assembled-Monolayer (SAM) onto different solid supports, i.e. gold, ITO and quartz. In the case of quartz and ITO sur faces we use a silane-end capped molecule, while for gold substrate we used a disulfide molecule.

The formation of the complex at the surface was successfully monitored by means of two different but complementary detection methods, i.e. Quartz Crystal Microbalance with dissipation monitoring (QCM) and UV-Vis-Nir absorption spectroscopy.

QCM results indicated that the functionalized molecule forms a rigid self-assembled film on gold as well as on ITO that strongly associates with the metal ions when added in the measurement chamber. The spectroscopic data for SAMs on quartz and ITO surfaces confirm the presence of the complex at the surface and allow to correlate the results to the acoustic shear waves investigations.

The construction of nano-assemblies on different surfaces allows the flexible choice of the experimental methodology for their characterization; at the same time diverse applications may be envisaged for the final device depending on the subst rate adopted.

POSTER C9

The (0001) sapphire surface as a possible template for pentacene thin film growth

Primoz Rebernik Ribic and Gvido Bratina

Polytechnic Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

We investigated the effect of deposition rate and substrate temperature on the morphology of ultrathin pentacene films on the (0001) miscut sapphire surface. Sapphire substrates were prepared by annealing in air at 1500°C for 72h. This resulted in a terrace-step morphology of the substrates with an average terrace width of 450nm and average terrace height of 2.1nm. Ultrathin films of pentacene were prepared by high vacuum deposition at a base pressure of $1\ 10^{-8}$ Torr. The morphology of thin films was studied by AFM. The density of pentacene islands increases with increasing deposition rate and decreases with increasing substrate temperature. At very low deposition rates, 3D growth of islands was observed, while for higher deposition rates the islands measured 1 monolayer in height. AFM images of early stages of nucleation indicate that at low deposition rates pentacene islands nucleate on terrace edges. Higher substrate temperatures result in somewhat elongated islands along the terrace edges. These observations suggest that terrace edges act as nucleation sites for pentacene islands. The (0001) sapphire surface could act as a template for pentacene growth.

POSTER C10

Calculated vibrational and Raman spectra of the neutral and negatively charged Mg-phthalocyanine

J. TOBIK

SISSA/ISAS, via Beirut 24, 34014 Trieste, Italy

Recent experiments by Delft group [1] reported metallic conductivity of K doped metallo-phthalocyanines (MPcs). The amount of doping electrons per molecule in the case of fullerenes was shown to be proportional to the frequency shift of the vibrational modes. Such experiment tool is very important for characterization of the charge state of molecules.

In this work we calculated by density functional theory vibrational and Raman spectra of the neutral and negatively charged MgPc molecule. Due to the two-fold degeneracy of the LUMO level the negatively charged molecule is Jahn-Teller active. The determination of the electron-vibration coupling constants determining Jahn-Teller effect are byproduct of our calculation.

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POSTER C11

TITLE?????????

Comisso Alessio (1), Gattinoni Chiara (2), De Vita Alessandro(1, 2)

(1)Department of Material Engineering, Universtity of Trieste
(2)Department of Physics, King's College London

Recent studies have revealed that theoretical simulations performed in conjunction wit scanning tunneling microscopy (STM) allows for unprecedented insight in complex molecular architectures.

To investigate formation mechanisms, chemical bonding and function of self-assembled supramolecular nanostructures we perform computer simulations using state of the art techniques at various levels of accuracy. A combination of classical and ab initio molecular dynamics is used to understand regular patterns experimentally observed in STM images and mechanisms that rule the self-assembly of the Extended TMA on Ag<111>.

POSTER C12

Stability and Migration of Metal Ions in G4-wires by Molecular Dynamics Simulations

M. Cavallari[a], A. Calzolari[a], A. Garbesi[a,b] and R. Di Felice[a]

a: National Research Center on nanoStructures and bioSystems at Surfaces (S3) of INFM-CNR, Modena, Italy
b: CNR-ISOF, Bologna, Italy.

The G-quartet [1] (Fig.1) is a planar macrocycle formed by the assembly of four guanines held together by a double ring of hydrogen bonds. It is the fundamental building block of the supramolecular structures formed: (i) by oligoguanylates and G-rich oligonucleotides in water and (ii) by lipophilic derivatives of guanosine in organic solvents. All such supramolecular objects are characterized by the presence of a helical stack of the basic tetrameric unit and of a row of cations filling the central cavity. Depending on their size, the cations are coplanar with G-quartets or sandwiched between them. In any case, metal cations are deemed essential for both templation and stabilization of this type of ordered supramolecular aggregates, called here G4-wires.

We present a Molecular Dynamics (MD) investigation of guanine quadruple helices based on classical force fields (NAMD code [2], AMBER force field [3]), addressing two basic issues: (i) the relative rigidity/flexibility of G4-quadruplexes of variable length and containing metal cations of different alkaline species; (ii) the dynamical behavior of G4-quadruplexes without cations inside. The dynamical trajectories are analyzed in terms of the time-dependent root mean square deviations, as well as in terms of statistical distributions [4].

In compliance with previous indications, our results suggest that monovalent alkali cations assist the stability of the quadruplex arrangement against disruption, on the few-nanoseconds time scale, in the order of increasing van der Waals radius (Fig.2). Whereas very short G4-wire fragments immediately unfold in the absence of coordinating metal ions or in the presence of tiny ions (e.g., Li^+), in agreement with the experimental evidence that empty short guanine quadruplexes are not formed in any synthetic conditions, our simulations show that longer empty helices do not discompose. This finding supports the possibility of producing long G4-wires with different guanine-cation stoichiometries than those routinely known. The classical trajectories allow us to identify different stationary axial sites for the different metal species, which are confirmed by complementary quantum calculations.

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Figure1: The G-quartet: the double ring of H-bonds is clearly shown.

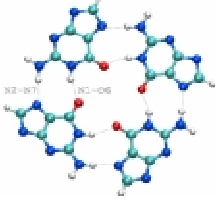
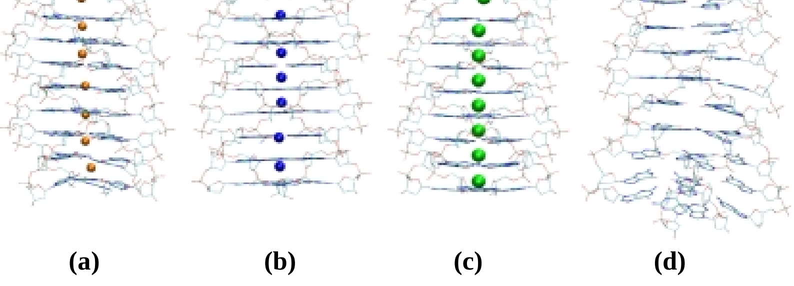


Figure 2: MD average structures of the 9-plane quadruple helices containing (a) Li^+ ions, (b) Na^+ ions, (c) K^+ ions and (d) no ions.


(a) **(b)** **(c)** **(d)**

POSTER C13

Polymer 1D photonic crystals by soft nanopatterning and deposition

Luana Persano, Elisa Mele, Andrea Camposeo, Pompilio Del Carro, Ripalta Stabile, Roberto Cingolani,
Dario Pisignano

National Nanotechnology Laboratory of Istituto Nazionale di Fisica della Materia-CNR and Scuola
Superiore ISUFI, c/o University of Lecce, via Arnesano I-73100, Lecce, Italy

Organic conjugated materials have attracted an increasing interest, since coupled or embedded in photonic crystals (PhCs) can provide new effective media for photonic applications. In particular, polymers exhibiting good performances of amplified spontaneous emission and gain cross sections over a broad spectral range are suitable for the realization of optically pumped laser devices. In order to provide the feedback required for lasing, non invasive lithographic and deposition tools have to be specifically implemented and developed, enabling patterning active conjugated materials without the deterioration of the optical properties .

We report on two complementary processing approaches, working at low temperature, for the realization of 1D PhCs polymer lasers relying on (i) planar distributed feedback geometries and (ii) integrated vertical -monolithic- microcavities, respectively. The impact of the lithography/deposition on the absolute quantum yield of organics was carefully investigated, allowing us to rule out the degradation of the emission upon processing. Organic lasers in the whole visible and in the near infrared range with both geometries were achieved, with thresholds of the order of microJ/cm^2 and lifetime of the order of 10^4 pulses, in air. The processing techniques are presented, and the possible applications of the different technologies for the perspective realisation of electrically-injected devices is discussed.

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POSTER C14

AC CHARACTERIZATION OF THE ELECTRICAL PROPERTIES OF ORGANIC THIN FILMS

M. Barra, M. Biasiucci, A.Cassinese, P.D'Angelo

CNR-INFM,Coherentia and Università di Napoli Federico II, Dipartimento di Fisica,Napoli, Italy,

Despite the great interest that many research groups have recently dedicated to the study of the electrical behavior of organic materials, the AC regime characterization of many of these materials is yet to be performed in detail. Actually, frequency responses up to the MHZ range can provide a deep insight about many electrical (i.e the dielectric response, the characteristic relaxation time, the charge carrier mobility, the charge carrier injection) and structural (glass and melting temperatures) properties. In this presentation, we report on AC measurements carried out on both insulating (polydimethylsiloxane - PDMS) and semiconducting (poly-alkoxyphenylthiophene and Rose Bengal) organic films, of interest for the application in low cost, innovative electronic devices such as thin film transistors and memories.
In particular, the impedance frequency response of simple PDMS films (thickness of about 5μm), as a function of temperature, has shown to be a non invasive and very high sensitive tool for the evaluation of glass transition temperature T_G. Such measurement is proposed alternatively to the Differential Scanning Calorimetry (DSC), based on a thermo-mechanical measurement, and R(T) measurement, requiring on its turn a preliminary doping procedure in the case of polymeric insulators, as Polydimethylsiloxane (PDMS) [1]. On the other hand, frequency measurements, as a function of an applied DC bias, performed on poly-alkoxyphenylthiophene and Rose Bengal films sandwiched between different conducting electrodes (silver, gold, aluminum, ITO) allow to investigate the intrinsic nature of the interfaces between metal and organic materials and the related charge carrier injection mechanisms. These studies, in combination with the DC characterization, can help to better clarify the interface role in the occurrence of peculiar electrical phenomena, such as the presence of conductance switching phenomena and bistable behavior [2].

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POSTER C15

Transport properties of regioregular doped and undoped poly-3-(4-alkoxyphenyl) thiophenes films

A. Cassinese[1],, M. Barra[1], M. Biasiucci[1],A. Roviello[2], A. Buono[2], G. Roviello[2]

CNR-INFM,Coherentia and Università di Napoli Federico II, Dipartimento di Fisica,Napoli, Italy,
Università di Napoli Federico II, Dipartimento di Chimica,Napoli, Italy

In this work, we investigated the electrical transport properties of doped and undoped regioregular poly-3-(4-alkoxyphenyl) thiophenes, where the alkoxy groups are $O\text{-}(CH_2)_{n-1}CH_3$ with n=1,4,6 and 8. Polymers of this class with n = 1, 6 and 8 have been already prepared [1],[2],[3], but they have a regioirregular constitution. The facile large scale synthesis of monomers with very high purity, starting from unexpensive reagents, the improved donor capability of the alkoxy chain in respect of the alkyl analogues and the benefic influence of bulky phenyl groups on the regioregular chaining of the thiophene rings are the most relevant reasons for choising this type of polymers. Furthermore, high molecular weight polymers, having high solubility in common organic solvents, are easily prepared by direct oxidation of the monomers, so avoiding the expensive procedure of their bromination and the use of Rieke metals or Grignard reagents, achieving also high regioregularities, extimed about 95%. The polymers have been extensively characterized by standard chemico-physical methods. They show behaviours that are strictly parallel to other regioregular 3- alkyl or 3- alkylphenyl substituted polythiophenes, widely described and used in literature, but their thermal stability is significantly higher. By UV-Vis and RX spectra it was clear that films as obtained by spin coating technique, already present the optimized properties. In fact they show an high spontaneous structural ordering without any additional treatment such as slow evaporation of the solvent, annealing, exposure to solvent vapours and so on. The film thicknesses are in the range of 1μm, with a smooth roughness (<1nm), as resulted by AFM investigations performed in tapping mode.

The electrical measurements have been carried out by using a cryogenic probe station where the environmental conditions, stability in air and possible hygro-scopicity, can be accurately controlled.

I-V current- voltage characteristics have been measured at room temperature both in planar and in transverse configuration, where the organic films have been sandwiched between different metal electrodes. In planar configuration, different samples have been investigated with channel length ranging from 100mm to 600nm. In this last case, electron beam lithography on gold electrodes in bottom contact configuration has been employed. In planar confinguration, for regioregular films, the resitivity is $(1,30\pm0,01)x10^{-9}$ and $(0,8\pm0,1)x10^{-6}$ for undoped and 1% fecl3 doped films respectively. The comparison between planar and transverse measurements shows that the resitivity is anisotropy remarking the well structured lamellar organization of the polymer chains in ab plane..The resistivity temperature dependence has also been analyzed by standard two probe techniques and compared with main theoretical electron transport models.

Furthermore, dielectric and AC conductivity measurements have been performed in the range 100 Hz-1MHz and in presence of a d.c field, in order to better investigate the dielectric properties and the nature of the interface between metal and organic films.

Finally, prototype filed effect devices have been fabricated. In all the devices, the field effect modulation provides an increase of the channel resistance R_{sd} for positive gate voltages, which is consistent with the fact that the carriers are holes. Measured mobility has a maximum aching a maximum value of $\mu\underline{=}10^{-3}cm^2/V*s$ in case of 3 % $FeCl_3$.

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POSTER C16

Towards a quantitative determination of the charge distribution in T6 films by Phase-Electrostatic Force Microscopy (EFM)

Cristiano Albonetti, Jean Françoise Moulin, Paolo Annibale and Fabio Biscarini

Consiglio Nazionale delle Ricerche (CNR)-Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Sez. di Bologna, Via P. Gobetti 101, I-40129 Bologna, Italy

Phase-Electrostatic Force Microscope (EFM) is used to evaluate the charge distribution in α-sexithiophene (T6) thin films deposited on SiO2/Si substrate. This measure is crucial in order to investigate the role of the charge distribution induced in OFET (Organic Field Effect Transistor) by the bias gate and to elucidate its role in the charge transport mechanism. T6 films grown layer by layer have been chosen. Surface charges can be observed via detecting the electrostatic force exerted between a biased conductive probe and a grounded sample. Thanks to the high sensitivity of Phase-EFM technique respect to the electric field variations, we are able to discriminate the surface potential of each single monolayer. In order to correlate the cantilever phase signal with the surface potential, we have modelled the electrostatic interaction of the tip-sample system by using prolate spherical coordinates for the tip-sample gap and Cartesian coordinates for the sample. The experimental data shows a decreasing trend of the surface potentials with the increase of the surface coverage. The surface density charge, calculated from the surface potential for each monolayer, is observed to decay in agreement with the demonstrated charge confinement at the second monolayer of the charge transport layer.

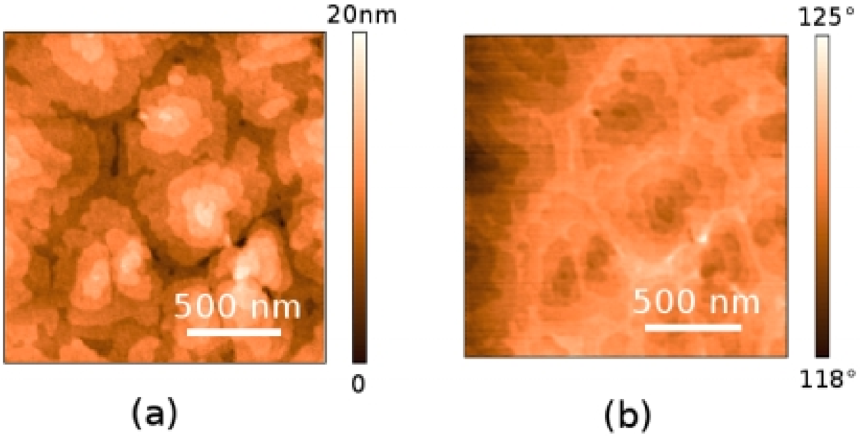

Figure: (a) Topographic image of T6 thin film, **(b)** Corresponding electrostatic phase image (Sample grounded and tip biased at +10V)

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POSTER C17

Odd-Even fluctuations of the charge injection across Self-Assembly Monolayers in Organic Field Effect Transistors

P. Stoliar†*, R. Kshirsagar*†*, M. Massi*†*, D. M. de Leeuw*§, *F. Biscarini*†

†CNR-ISMN,Via Gobetti 101, I-40129 Bologna, Italy
§Philips Research Laboratories, High Tech Campus 4, NL-5656 AA, Eindhoven, The Netherlands

We address the problem of the injection barrier in an organic field effect transistor. The injection interface in pentacene field-effect transistor is modulated by alkanethiol monolayers of chain length n self-assembled on the gold source and drain electrodes. The charge carrier mobility, μ, exhibits fluctuations correlated with odd-even n. For $n < 8$, μ increases by one order of magnitude due to the decrease of the pentacene hole injection barrier and the improved molecular order at the organicmetallic interface. For $n \geq 8$, μ decays exponentially as the charge injection across the alkanethiol monolayer completely governs the transistor response. Our results show that

i) the transistor is sensitive to submolecular details at the interface between Au and pentacene;

ii) charge injection across the interface occurs by through-bond tunneling mediated by the alkane-thiol layer.

We invoke a super-exchange mechanism for charge transport between Au and pentacene, to explain the sensitivity of the FET to the coupling between pentacene HOMO and the terminal methylenemethyl bond in the alkanethiol chain. Our results show that the pentacene transistor may be operated as a gauge for probing charge transport across single monolayers, thus bridging together molecular and organic electronics.

POSTER C18

Field effect transistors with organic semiconductors assembled from a nano composite template

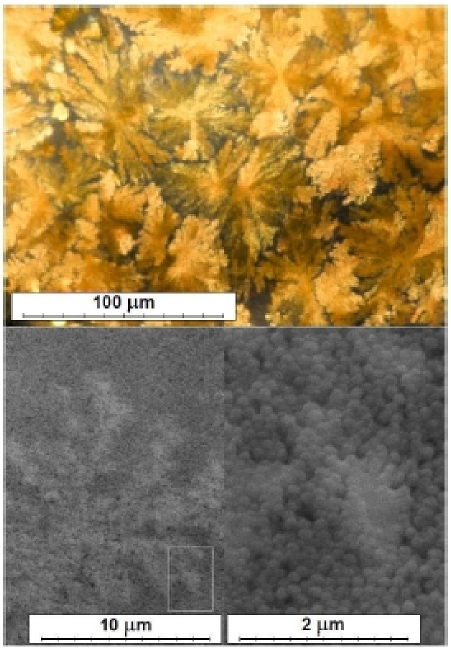
Chiara Dionigi (1), Pablo Stoliar (1), William Porzio (2), Silvia Destri (2), Massimiliano Cavallini (1),
Ivano Bilotti (3), Aldo Brillante (3), Fabio Biscarini (1)

(1)Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati , Via P. Gobetti 101, 40129 Bologna, Italy
(2)Consiglio Nazionale delle Ricerche , Istituto per lo Studio delle Macromolecole, Via Bassini 15, 20133 Milano, Italy
(3) Dipartimento di Chimica Fisica e Inorganica and INSTM-UdR Bologna, University of Bologna, 40136 Bologna, Italy

Organic field effect transistors (OFET) are of great interest for the development of organic electronics, such as digital logic circuits and active matrix display back-panels, and bio-diagnostics devices.
We demonstrate, operating field effect transistors where the semiconducting material self-organization is controlled by dielectric bead array , leading to the growth of large interconnected domains
A colloidal composite made of polystyrene beads (PS) and tetrahexyl-sexithiophene (H4T6) is deposited with a micro-pipette into the channel of a bottom-contact field effect transistor. The beads self-organize into a network whose characteristic distances are governed by their packing. The semiconductor molecules crystallize in the interstitial voids, leading to the growth of large interconnected domains (fig 1). Depending on the bead size and the ratio between H4T6/PS, the percentage of the different phases in the polymorph can be controlled. In the transistors where H4T6 metastable “red phase” is the largest, the device response and the charge mobility are comparable to those of sexithienyl thin films grown by high vacuum sublimation.
The method we propose for depositing the active layer from bead carriers is completely general for soluble semiconductors, and could give significant advances on OFET fabrication by solution processing techniques. The transfer characteristics, Raman and XRD properties of FETs fabricated with H4T6/PS composite are presented.

This work is supported by the EU Integrated Project NAIMO (NMP4-CT-2004-500355).

Figure 1: (top) Optical image of dendritic domains under polarized light in a dried colloidal composite made of H4T6 and 150 nm PS; (bottom) SEM images of a domain (left) and a zoom of it (right).



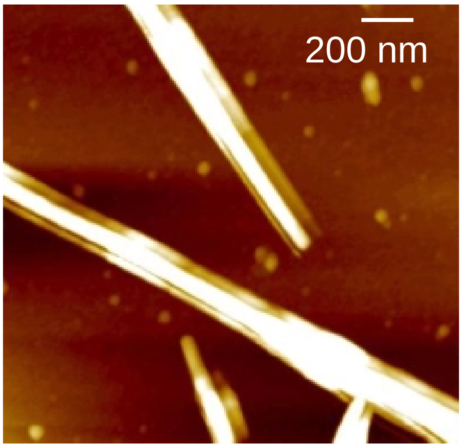
POSTER C19

Self-assembly of hexa-*peri*-hexabenzocoronene / perylene-bis-dicarboximide blend films from solution: controlling the interplay of interaction forces among molecule, solvent and substrate

Vincenzo Palermo[a], Andrea Liscio,[a] Desirée Gentilini[b], Fabian Nolde[c], Jishan Wu,[c]
Andreas Herrmann,[c] Klaus Müllen[c*], Paolo Samorì[a,b*]

[a] Istituto per la Sintesi Organica e la Fotoreattività - Consiglio Nazionale delle Ricerche
Via Gobetti 101, 40129 Bologna, Italy.
[b] Nanochemistry Laboratory, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université Louis Pasteur, 8, allée Gaspard Monge, F-67083 Strasbourg (France)
[c] Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55124 Mainz (Germany)

Controlling the self-assembly of conjugated molecules at surfaces is important to improve the performance of (opto)electronic devices. We report on the self-assembly from solutions at surfaces of perylene-bis-dicarboximide (PDI), an electron acceptor widely used for the fabrication of solar cells.[1]
By tuning the experimental conditions, including the solution concentration, the solvent type, the substrate polarity and the fine chemical structure of the molecule, it was possible to form different architectures as needles (see figure) and ultra thin layers. A Scanning Force Microscopy study of the different supramolecular architectures revealed that the self-assembly governing the formation of such structures is ruled by the competition between molecule-molecule, molecule-solvent and molecule-substrate interactions. Moreover, by co-depositing PDI and hexa-*peri*-hexabenzocoronene (HBC), complex structures composed by a first layer of PDI nanocrystals with lengths >3000 nm and widths <100 nm, partially covered by isotropic HBC aggregates were obtained. Preferential dewetting of HBC on the PDI nanocrystals was observed, indicating that molecule-molecule interactions override the molecule-substrate ones. The phase segregation of the two molecules in this complex morphology was confirmed by their different local surface potentials, due to the electron acceptor and donor character of PDI and HBC, respectively, as monitored by Kelvin Probe Force Microscopy.



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POSTER C20

Molecular Order and Surface Characterisation of Nanografted Structures into Self Assembled Monolayers using CT-AFM

D. Scaini[1,2], J. Liang[4], M. Castronovo[1,2], M. dell'Angela[2], S. de Franceschi[5], L. Casalis[1], G. Scoles[1,3,4]

[1]Sincrotrone Trieste, Trieste, Italy
[2]Dipartimento di Fisica, Universita' di Trieste, Trieste, Italy
[3]Scuola Superiore di Studi Avanzati (SISSA), Trieste, Italy
[4]Princeton University, Chemistry Department, Princeton , NJ
[4]TASC-INFM, Trieste, Italy

Conductive Tip AFM (CT-AFM) is commonly used for electrical characterisation of organic and inorganic surface systems. One of the more promising applications concerns the study of metal-molecule-metal junctions: Understanding the transport properties of these key systems is in fact of great importance for the advancement of both organic and molecular electronics.

Despite the non negligible number of experimental data in this field, however, the accumulated data sets are often not consistent with each other, due to the scarce reproducibility of the metal tip-molecule contact at a microscopic level. Nanografting, an AFM-assisted nanolithography technique, has been proved to be a very useful method to compare transport properties of different molecules on the same substrate with the same probing tip. Differential measurements of this kind have been useful to distinguish conductivity differences between molecules with subtle structural differences.

We will discuss here in detail the case of patches of alkyl- or aromatic-thiols nanografted into a matrix of alkyl-thiol self-assembled monolayer (SAM) made of different length molecules. By differentially comparing the “conductivities” of different molecules we will show that the discrepancies present in the literature are due to the fact that the metallic tip of the CT-AFM gets invariably coated by the molecules of the monolayers so that most measurements relate to the tunneling of current through TWO monolayers instead of one.

We will also address specifically the very important point of the influence of the degree of order in the nanografted patches and the surrounding SAM on the transport properties of the measured metal-molecule-metal junction. We will show that, if the tip of the CT-AFM

Is smaller than the average SAM domain our technique allows the unequivocal determination of the SAM “defect free conductivity”

POSTER C21

Adaptive Atomic Force Microscopy

M.Basso (1,3), B.Tiribilli (2,3), M.Vassalli (2,3)

(1) DSI – Università di Firenze
(2) ISC Firenze – CNR
(3) CSDC – Università di Firenze

Atomic Force Microscopy (AFM) is an experimental technique allowing to image the surface of a sample with a resolution up to few nanometers. Based on a simple measuring concept, AFM does not need vacuum chambers or special sample treatment in order to characterize the surface topography and it is therefore a widespread instrumentation in the field of material science and
nanotechnology. After its invention in the ‘80s, AFM has greatly improved and it has began moving towards industrial applications. This trend resulted, in the last years, in a greater attention also to usability and reliability of the measuring system. Besides several improvements aimed to this purpose have been already introduced by the world leading AFM manufacturers, there are still some irksome parameters the user has to deal with using standard microscopes.

The AFM probe, a micron-sized cantilever with a sharp tip on the top, bends elastically due to the contact with the sample; topographic information about the surface are recorded by performing a planar (XY) scan and measuring the cantilever deflection or, often, introducing a feedback system that keep constant the tip-sample distance by moving the sample in vertical (Z) direction. The performances of the whole measuring system are mainly related to the efficiency of this control ring at the selected scanning speed or, in other words, the user has to tune correctly the feedback gains (typically proportional and integral gains) as a function of the scanning frequency.

The aim of our work has been to eliminate the need for this obscure procedure, letting the user dealing only with functional requirements. We designed and implemented on a PC based real-time controller an AFM driving strategy where the user should choose only the error level, in nanometers or in force, completely forgetting parameters related to the implementation details.

Feedback design and synthesis

The first step was a black box identification of the piezoelectric scanner. By exploiting frequency domain identification technique it provides a mathematical model of the AFM dynamics. Once the model is known it is possible to synthesize an optimal control algorithm based on robust controllers techniques. We decided to implement a H¥ robust control on a PC running Linux patched for Real Time operation (RTAI). This controller strategy improved the bandwidth of the system allowing scanning rate five time faster the conventional PID controller. In addition to this, it is possible to choose the feedback parameters only on the base of the identified model, without the need to change them during measurement operations.

Adaptive speed

Exploiting the flexibility of the hardware platform, we were also able to introduce a non-stationary working mode, were the speed of each scanning line is automatically chosen taking into account the sample topography. Once selected the error threshold to be achieved, the controller drives the system, changing the scanning speed in order to reach the desired value. This strategy clearly allows remaining under the maximum desired error, but it also guarantees to select the higher speed that fulfill this requirement, minimizing the total scanning time for a specific functional constraint.

POSTER C22

Confocal Raman-AFM, a new tool for materials research

U. Schmidt, F. Vargas, W. Ibach, Sabine Hild[1], J. Müller, J. Koenen, K. Weishaupt, and O. Hollricher

WITec GmbH, Hörvelsinger Weg 6, 89081 Ulm, Germany, www.witec.de
[1]*Dept. of Experimental Physics, University of Ulm, Albert Einstein Allee,89075 Ulm, Germany*

Characterization of heterogeneous systems on the nanometer scale continues to grow in importance and to impact key applications in the field of materials science (phase segregated systems), nanotechnology (molecular electronics), and catalysis (single site catalysts). Detailed information on this length scale is necessary to test and evaluate advanced materials. However, some details about the phase-separation process in polymers are difficult to study with conventional characterization techniques, due to the inability of these methods to chemically differentiate materials with good spatial resolution, without damage, staining or preferential solvent washing.

The CR-AFM combines a high resolution confocal optical microscope with Raman spectrometer and an Atomic Force Microscope. Using this instrument, the high spatial and topographical resolution obtained with an AFM can be directly linked to the chemical information gained by Confocal Raman spectroscopy.

To demonstrate the capabilities of this unique combination of measuring techniques, thin films of polymer blends on glass substrates have been characterized. AFM measurements reveal the structural and mechanical properties of the films. Scratching the films with the AFM cantilever gives insight to the thickness of the films. This varies from 20 –100 nm. Even on 20 nm thick films, the Raman spectra show the presence of a specific chemical compound (bond), enabling the possibility to chemically identify the different compounds of the blends in a decent time frame.

Examples from the system PMMA-SBS will be presented.

POSTER C23

CESYRA : in-situ NEXAFS characterization of sp-rich cluster assembled carbon film

L. Ravagnan[1,4], P. Piseri[1,4], C. Lenardi[2,4], G. Bongiorno[1,4], D. Bandiera[1,4], E. Salis[3,5], P. Milani[1,4]
M. Coreno[6,7], M. de Simone[6]

[1] INFM-Dipartimento di Fisica, Università degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy
[2] INFM-Istituto di Fisiologia Generale e Chimica Biologica, Via Trentacoste 2, 20134 Milano, Italy
[3] INFM-Dipartimento di Ingegneria Nucleare, Politecnico di Milano, Via Ponzio 34/3, 20133 Milano, Italy
[4] Centro Interdisciplinare MAteriali ed Interfacce NAnostrutturati (CIMAINA), Università degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy
[5] Center of excellence for NanoEngineered MAterials and Surfaces (NEMAS) - Politecnico di Milano, Via Ponzio 34/3, 20133 Milano, Italy
[6] INFM, TASC Laboratory, 34012 Trieste, Italy
[7] CNR-IMIP, Area della Ricerca di Roma 1, 00016 Monterotondo Scalo (RM), Italy

Linear carbon chains with sp coordination (also known as carbynoid structures) represent an elusive form of carbon interesting for both nanoscience and astrophysics. Although many physical and chemical routes have been proposed to synthesize carbynoid structures both in the solid state and in the gas phase, stabilizing molecular groups have always been used to avoid interchain crosslinking.

Recently some of us have demonstrated that it is possible to synthesize by supersonic cluster beam deposition an sp-rich pure carbon system. This has been shown by Raman spectroscopy characterization, which is a very sensitive technique to detect sp-chains presence in a carbon system, but that unfortunately does not allow to determine the fraction of the film consisting in sp carbon.

For this reason we have used a high intensity cluster source (PMCS: Pulsed Microplasma Cluster Source; developed by the Molecular Beams Laboratory at the University of Milano, Italy), coupled to an apparatus designed to allow the study of inner-shell X-ray absorption spectroscopy both on in situ cluster assembled films and also free clusters in a molecular beam (Project CESyRa: Cluster Experiment with Synchrotron Radiation).

As well as Raman spectroscopy, NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy is an effective technique for identifying sp-hybridised carbon atoms. NEXAFS has the further advantage of enabling an evaluation of the sp fraction, even though in an amorphous system the sp contribution could be partially concealed by the prominent sp^2 peak.

Combining Raman and NEXAFS characterization we have thus been able to estimate the content of sp species in the in situ grown nanostructured carbon films. This result opens new perspectives in the understanding of the structure of nanostructured carbon films deposited by supersonic cluster beam deposition, and sheds new light on the nature of the precursor carbon clusters.

POSTER C24

Functionalisation of Carbon Nanohorns

Carla Cioffi (a), Stéphane Campidelli (a), Fulvio G. Brunetti (a), Moreno Meneghetti (b) and Maurizio Prato (a)

(a) Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy.
(b) Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1 I-35131 Padova, Italy.

Nanometer-scale structures are under active investigation for producing innovative materials, composites, and electronic devices of greatly reduced size. Single Wall Carbon Nanohorns (SWNHs) are a new class of carbon-based nanomaterials derived from SWNTs.

A few years ago, we demonstrated that the functionalisation of carbon nanotubes via the 1,3-dipolar cycloaddition allows to increase their solubility in organic solvents as well as their processing ability. In the same way, organic functionalisation of SWNHs may open new doors for the use of nanohorns in material science and may also increase their solubility in water for biomedical applications.

Herein, we describe the functionalisation and characterisation of single wall nanohorns. The functionalized nanohorns were characterised by Raman and UV-Vis-NIR spectroscopies as well as electron microscopy and thermogravimetry. The nanohorn derivatives present a good solubility in the common organic solvents. TEM and SEM images show that the nanohorns are aggregated forming the characteristic secondary nano-structures.

POSTER C25

Single Wall Carbon Nanotubes Functionalized with Dendrimer

S. Campidelli,[a] C. Sooambar,[a] E. Lozano Diz,[b] C. Ehli,[c] D. M. Guldi[c] and M. Prato[a]

[a]Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy.
[b]Instituto de Catalisis y Petroleoquimica Campus de la Universidad Autonoma, C/ Marie Curie 2, 28049 Madrid, Spain.
[c]Institute for Physical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany.

Nanometer-scale structures are under heavy investigation for producing innovative materials for composites, electronic, sensing, and biomedical applications. In particular, Carbon nanotubes (CNTs)[1,2] are fascinating nanostructures with exceptional mechanical, electronic, and optical properties. However, processing of CNTs are severely limited because of the difficulties of purification, manipulation and low solubility.

The covalent functionalisation of nanotubes with organic pendant groups[3-5] permits to improve their solubility and thus decrease CNTs aggregation. Specially, attachment of dendrimers on the nanotube sidewalls seems a promising method which allows the combination of the properties of the dendrimers with thus of CNTs.

Here, we describe the functionalization of SWNTs with PAMAM dendrimers[6] and porphyrins. The resulting compounds have been characterized by several methods and their photophysical properties have been investigated.

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POSTER C26

Carbon Nanotube carriers for fabrication of ordered CNT networks

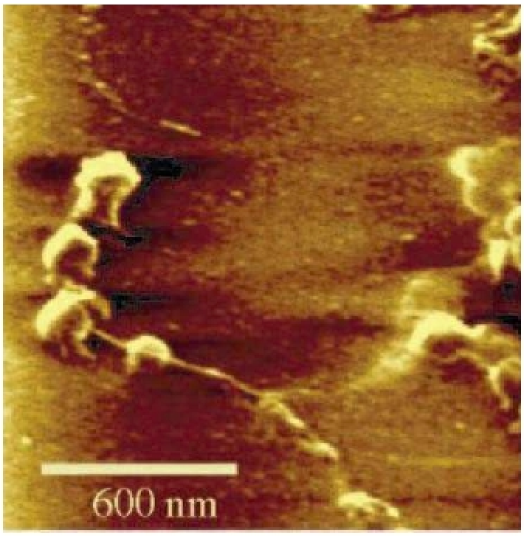
Chiara Dionigi, Pablo Stoliar, Giampiero Ruani, Massimiliano Cavallini , Massimo Facchini,
Fabio Biscarini

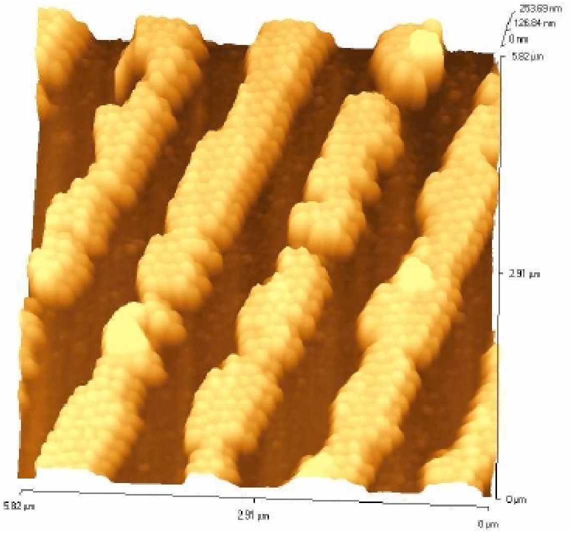
CNR- Istituto per lo Studio dei Materiali Nanostrutturati, ISMN Research Division, Bologna, Italy

CNTs are materials of great relevance for their unique mechanical and electrical properties. However, they are not easy to process by sustainable solution-based techniques.

Our approach is to integrate CNT and polymer beads into nanosized composites to be used as a new class of building blocks for the fabrication of ordered CNT networks for sensors and electronics devices by printing and microfluidics techniques. We demonstrate that monodisperse polystyrene beads strongly interact with carbon nanotubes (CNT) bundles (see Figure). Hydrophobic interactions anchor CNTs on the beads surface. CNT/bead composites can be processed in fludics conditions (right fig.) to yield geometrically defined structures with mesoscopic length scales. By exploiting the spherical shape of the carriers a close packing structure infilled with CNTs is formed. The removal of the polymer carriers by a suitable solvent yields a connected CNT network that maintains the geometrical structure in 3D of the assembled beads. The electrical and spectroscopic properties of the CNT networks fabricated in this manner are presented.

This work is supported by EU NMP-IP Project CANAPE.





POSTER C27

A simple methodology to disperse and de-bundle SWNT using organic solvents

SILVIA GIORDANI

Trinity College Dublin, School of Physics, College Green, Dublin 2, Ireland

The ability to miniaturise devices has completely changed our society, and modern technology is constantly pushing towards smaller and lighter devices with enhanced and more diverse functionalities. Single-walled carbon nanotubes (SWNTs) display unique structures and remarkable physical properties and are promising candidates for the realization of smart nanomaterials. They have nanoscale dimensions, and can be modified through covalent bonding of functional organic molecules, opening the way to structural materials of high technological importance. One of the major bottlenecks to applications is their aggregation into bundles. Many methods have been suggested to de-bundle the SWNTs, including both covalent functionalisation and non-covalent funtionalisation with surfactants, polymers and macromolecules. These methods have their advantages but the ideal situation must be to dissolve and de-bundle the SWNTs in an appropriate solvent at concentrat ions that are useful for their implementation in applications. In this work I will show our simple methodology to disperse and de-bundle SWNT using organic solvents as dispersants. Using Atomic Force Microscopy we observe the bundle diameter distribution to decrease dramatically with concentration. Near-infrared Absorption and Emission Spectroscopy were carried out on all solutions confirming an increase in the population of individual nanotubes with decreasing concentration.

POSTER C28

Ab-initio ballistic conductance with spin-orbit coupling

A. Dal Corso (1,2), A.N. Smogunov (1,2,3), and Erio Tosatti1 (2,4)

(1) SISSA, Via Beirut 2/4, 34014 Trieste (Italy)
(2) DEMOCRITOS–INFM, Unit`a di Trieste, Via Beirut 2/4, 34014 Trieste (Italy)
(3) Voronezh State University, University Sq. 1, 394006 Voronezh (Russia)
(4) ICTP, Strada Costiera 11, 34014 Trieste (Italy)

Ballistic conductance ab initio calculations in heavy metal break junctions require a very accurate description of the nanocontact electronic structure near the Fermi level, in turn quite sensitive to relativistic effects and particularly to spin-orbit coupling. The complex k-vector approach proposed by Choi and Ihm [1] for calculating the ballistic conductance of open quantum systems within the Landauer-B¨uttiker approach is generalized to fully relativistic ultrasoft pseudo-potentials [2] in order to deal with ballistic transport in presence of spin-orbit coupling.

As test cases we present the complex k-vector electronic structure of a perfect monatomic Pt wire, and the ballistic conductance of a Pt wire with an idealized nanocontact consisting of a single strained bond. In these cases we compare the fully relativistic and the scalar relativistic results, highlighting the net effect of spin orbit.

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POSTER C29

CATALYST FILM ACTIVATION FOR SURFACE-BOUND CVD OF CARBON NANOTUBES

S. Hofmann (1), C. Mattevi (2), C. Cepek (2), M. Cantoro (1), S. Pisana (1), A. Parvez (1)
C. Ducat i(3), A. C. Ferrari(1), M. Sancrotti (2), A. Goldoni (4), J. Robertson (1)

(1) Electrical Engineering Division, University of Cambridge, UK
(2) CNR - Istituto Nazionale per la Fisica della Materia, Laboratorio Nazionale TASC, Trieste, Italy
(3) Department of Materials Science and Metallurgy, University of Cambridge, UK
(4) Surface Science Division, Sincrotrone Trieste S.C.p.A., Italy

Bottom-up device fabrication based on nanoscale building blocks, such as carbon nanotubes (CNTs), not only requires their scaleable, deterministic synthesis, but also, often more importantly, their controlled assembly. Surface-bound chemical vapour deposition (CVD) can be combined with lithographic catalyst prepatterning and epitaxial or electric field based alignment, which makes it currently the most promising technique for economic, hierarchical CNT device integration. This approach, however, exposes the substrate to the CNT growth atmosphere, which creates a need for less aggressive, low temperature processing conditions and requires a more detailed understanding of catalyst support and precursor interactions. It is commonly assumed that the catalyst metal forms a liquid intermediate and that bulk catalyst effects dominate CNT growth dynamics. Calculations of size-corrected melting points and carbon saturation often indicate minimum CNT synthesis temperatures >500^{o}C, seemingly incompatible with the 400-450^{o}C ceiling temperature of present back-end CMOS technology.

We introduce different catalyst preparation and patterning techniques to achieve scaleable sub-100nm accuracy on planar as well as more unusual substrate geometries, such as AFM cantilevers and fuel cell membranes [1]. We analyse catalyst reconstruction and sintering upon temperature elevation and in particular show how different atmospheres influence the de-wetting and activation of solid transition metal films on Si/SiO_2. We present in-situ XPS/UPS of the chemical state of the catalyst and its interaction with the CVD atmosphere. We report single wall CNT CVD at temperatures below 450°C from undiluted C_2H_2 and demonstrate field effects in as-integrated CNT FETs [2]. We suggest that surface, rather than bulk catalyst effects, dominate CNT growth kinetics for low temperature, surface-bound CVD and analyse the potential narrowing of the chirality distribution. Our finding that a liquid catalyst eutectic is not a necessity extends to catalytic growth of anisotropic nanostructures in general [4].

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