Attempting to maximize singlet fission by tuning the interchromophore coupling

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Singlet fission is a process in which a chromophore A in an excited singlet state (S_1) transfers part of its excitation energy to a neighbouring chromophore B in the ground state (S_0) and both are converted into triplet excited states (T_1) [1,2]:

$$A(S_1) + B(S_0) \rightarrow A(T_1) + B(T_1).$$

The process represents an opportunity to improve the solar energy conversion efficiency in photovoltaic devices. In fact, a sensitizer capable of quantitative singlet fission may generate two charge carrier pairs per absorbed photon in a semiconductor material.

The efficiency of singlet fission depends on the interaction between the two chromophores, which in turn is highly sensitive to their relative distance and orientation. Detailed investigations on the optimal mutual dispositions of the two chromophores are therefore strongly needed for the development of singlet fission materials.

We propose here a computational strategy to select the most favorable dimeric geometries for singlet fission and to test their suitability by simulating the excited state dynamics. For the first step, we present a diabatization procedure which allows to compute the electronic coupling between the initial and final state of the process in a semiempirical context. For the excited state dynamics simulation, we use a semiclassical trajectory surface hopping approach with "on the fly" semiempirical calculation of electronic energies and wavefunctions [3]. Performing the simulation of the excited state dynamics is particularly important not only to determine the singlet fission quantum yield, but also to identify competing processes and other deficiencies of the selected chromophore [4].

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Time resolved approach to the photodeactivation mechanisms of NSAIDs

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Our research aims to investigate the photophysics and the photoreactive paths activated in non-steroidal anti-inflammatory drugs' (NSAIDs) upon photon absorption in order to assess whether in-silico simulations can help to predict their photostable [1] or phototoxic nature.

To this purpose, we have first modelled the absorption spectra of NSAIDs, such as aspirin, carprofen, naproxen and ibuprofen in gas phase with the time dependent density functional theory (TD-DFT) [2] computational protocol. The most probable photophysical deactivation mechanism of the excited molecules has been investigated with the help of semi-classical dynamics simulations, performed with the surface-hopping algorithm incorporating spin orbit coupling [3].
Higher chances of producing phototoxic species are expected the longer the lifetime of the excited states, so the key behind the photostability of a drug is the accessibility of internal conversion funnels to reach the ground state in an efficient manner. These simulations allowed us to unravel that large molecules usually stay excited in the triplet manifold and smaller decay easily to the ground state.

Our goal is to translate the deactivation mechanisms in to a phototoxicity alert that could be introduced at early stages of the drug discovery process to help mitigating the risks associated with their exposure to light.

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Azide anion confined inside carbon nanotubes: quantum chemical study and molecular dynamics potential

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The exceptional energy difference between single, double and triple nitrogen-nitrogen bonds makes polynitrogen compounds promising candidates as high energy-density materials.
Recent discoveries[1,2] have shown that the synthesis of such molecules is now a reality, although the difficulty for their storage still remains an issue.
Indeed, such compounds are generally highly reactive, in particular at ambient conditions, and a major challenge is to find ways to improve their stability.
A possible approach is their confinement inside nanostructures of various types, for instance carbon nanotubes, such that the restricted space within the cavity and the host-guest interactions favour stabilization.
In this work we present an in-depth investigation of the confinement of the azide anion, a common precursor in the synthesis of larger nitrogen clusters, inside carbon nanotubes of different sizes and lengths.
In particular, quantum chemical calculations (using both wave function and density functional methods) of interaction energies, relaxation effects and an analysis based on natural bond orbitals will be presented along with a study of the effects on these properties with respect to the diameter and length of the nanotubes[3].
Moreover, preliminary results of molecular dynamics simulations will also be presented, in particular highlighting the implementation of the improved Lennard-Jones potential[4] in the DL POLY 4 program package.
A specific model potential will also be introduced, which treats explicitly the induction effects due to the presence of the excess charge on the nitrogen species, which allows for an analysis of the interaction types involved between the nanotube and the azide anion and a direct comparison to the quantum-chemical study.

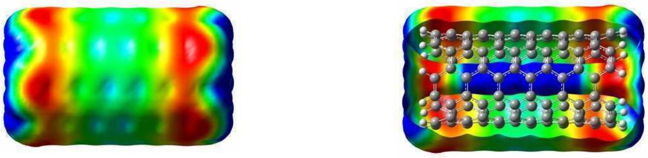

Figure 1. MESP of a CNT(5,5) perturbed by the presence of the azide anion.

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The role of theoretical modelling of nano-oxide materials: silica, titania and titanosilicates

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Properties of nanomaterials are known to be size dependent and generally are very different from those of the corresponding bulk. Such behaviour, which is strongly system and structure dependent, allows one to tune material's properties by varying their dimensions. This tunability opens up many possibilities in nanotechnology for manufacturing materials with tailored properties for specific applications. Thus, understanding size-dependent properties of nanoparticles and mechanisms taking place at the nanoscale is fundamental for the improvement of existing materials and for the designing of more efficient and optimized ones. However, the synthesis of nanomaterials and their experimental characterization is difficult, especially for very small systems. Here, theoretical modelling plays a fundamental role in the characterization of small nanoparticles for both helping experimental interpretation and predicting novel and potentially synthesizable materials with new properties.

Here we focus on modelling of titania, silica and titanosilicate based materials because of their technological and environmental importance as they are employed in heterogeneous (photo-)catalysis, electronics and gas sensing to cite a few [1-3]. For such systems, we firstly performed global optimization studies in gas-phase and water containing environments in order to identify the structures of nanoparticles. Secondly, we studied structural, energetic and electronic size-dependent properties of such nanoparticles as well as their reducibility, extrapolating up to the bulk macroscopic level in some cases. For such characterization we used accurate quantum mechanical methods based on Density Functional Theory (DFT). Our results point to a series of important predictions, such as for instance: (i) the crystallinity of titania nanoparticles, which is the key property for the photoactivity of such material, is predicted to emerge when nanoparticles become larger than 2.0-2.5 nm [4]; (ii) the mixing of titania and silica to form titanosilicates, which are an important class of materials used in industry as catalyst, is found be thermodynamically favourable at the nanoscale, contrarily to the bulk [5]; (iii) the hydration of silica and titania nanoclusters, which plays an important role in the aggregation and nucleation process during the synthesis of larger nanoparticles, is controlled by the environmental factors such as temperature and presence of water as predicted from calculated phase diagrams [6].

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Computational approach to aluminum biochemistry and development of new chelation strategies

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Aluminum is the third most abundant element on Earth's crust; however, its chemical properties prevented its utilization in the biochemical cycles of living organisms. In the last Century, human intervention has made such metal so highly (bio)available that it is often said that we are living in "The Aluminum Age" [1], raising justified concerns about the potential toxic role of Al(III) in the human body.

Due to the complex features of this exogenous ion that make experimental procedures a challenging task, *state-of-the-art* computational approaches would help to unveil the molecular basis of the interactions of aluminum in the biological environment.

The goal of this project is to investigate the potential detrimental effects of this metal with respect to different bioligands from a thermodynamic point of view [2], by means of the evaluation of binding affinities and chemical bond and molecular properties in aqueous solution.

Moreover, we developed and applied a computational protocol, based on different approaches (Fig. 1), suitable for the design and tuning of new and efficient chelating agents aimed to improve the removal of this exogenous ion.

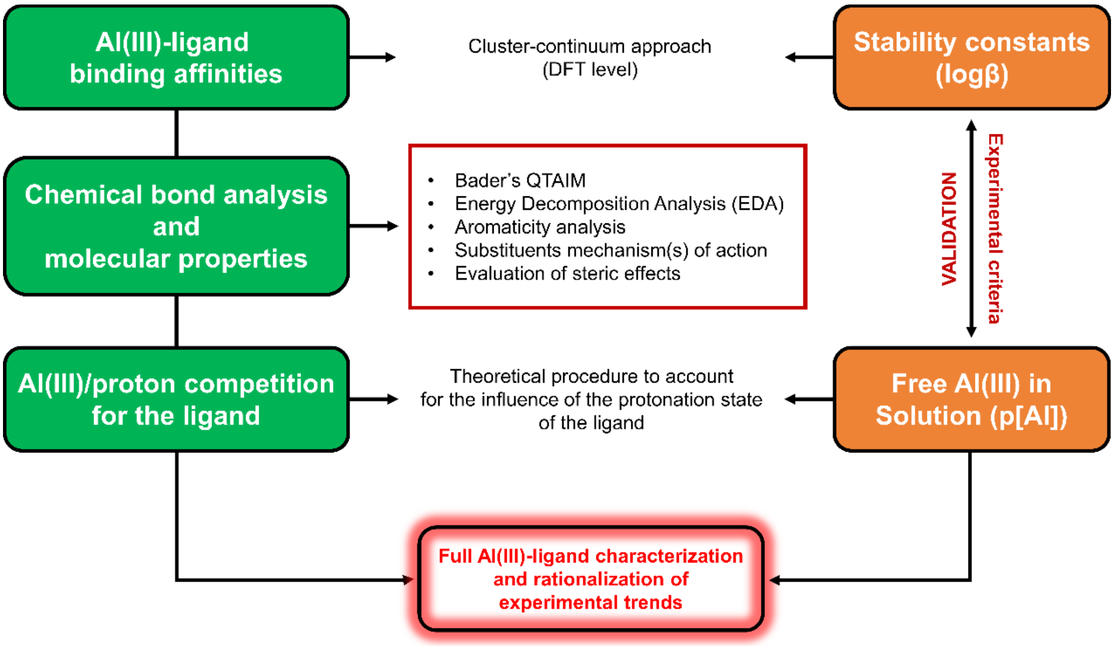

Figure 1. Schematic representation of the computational protocol developed in our work.

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Collision induced reactions of 5-bromouracil hydrated clusters

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Previous works have established the importance of the interaction biomolecule –water environment in determining molecular structure and function[1], molecular recognition[2] and the fidelity of DNA replication itself[3]. Already Watson and Crick indicated tautomerization as the main cause of DNA mispairing[4]. The incidence of such mispairing, according to Topal and Fresco, may be enhanced, among other factors, in presence of base analogues, as 5-bromouracyl (5BrU)[5]. Is that true? Here we present how, by means of experimental and molecular tools, we have tried to answer this question. The experiments, performed at the ARIBE facility[6], involve collisions between neutral clusters of $[5BrU]_m(H2O)_n$ and a C^{4+} ion at 36 keV . The computational approach to such a system consisted of both static calculations, aiming to sample the potential energy surface of different possible reactive species at m062x/6-311++g(d,p) level of theory[7], and of Born-Oppenheimer molecular dynamics (BOMD)[8] using the same functional and a SVP basis set, where we have simulated entire sequences of the system after energy has been deposited with an ionizing collision. Figure 1 presents one of the mentioned sequences obtained from the MD. The combination of both results helped us give an interpretation of the fine chemistry involved in the fragmentation processes occurring in the collision camera, which lead to the formation of unexpected extra-hydrogenated fragments.

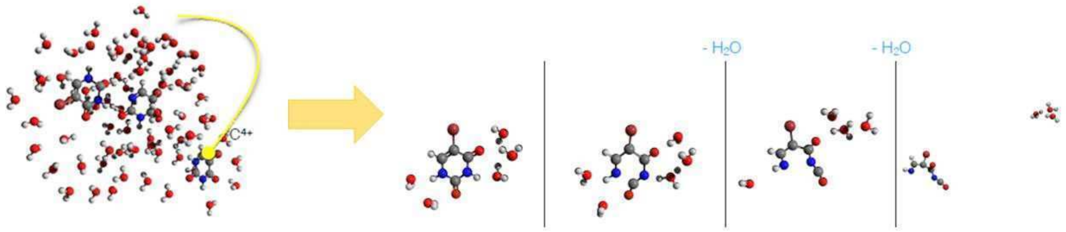

Figure 1. Snapshots from one of the BOMD trajectories.

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Trichromium extended metal atom chains from a multiconfigurational perspective

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Extended metal atom chains (EMACs) consist of three to eleven metal atoms hold together in a virtually linear way by multidentate organic ligands and as such can be considered as nanowires. Experimental and theoretical studies have shown that these compounds can indeed be used to electronically connect two electrodes. Given the fact that in most EMACs the metal chain is formed by transition metal ions with many unpaired electrons, one may expect that the electronic structure reflects a considerable multiconfigurational character. Here, we discuss different aspects of the electronic structure of the Cr_3 EMACs with emphasis on the influence of the axial ligands on the geometry and bond character of the Cr_3 unit. We combine multiconfigurational approaches such as CASPT2 and GASSCF with effective Hamiltonian theory to derive relatively simple models from the highly complicated multiconfigurational wave functions.

Computational models to improve photosensitizers for photodynamical therapy

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The design of efficient photosensitizers to be used in photodynamic therapy (PDT) can be strongly supported by theoretical modelling. In this presentation, I will show our efforts to find novel photosensitizers and improve existing ones, based on BODIPY derivatives and Temoporfin, respectively. BODIPY derivatives have recently emerged as potential photosensitizing compounds which can undergo singlet-triplet interstate crossing – a photophysical process which is key to the production of reactive singlet oxygen in PDT. Based on the comprehensive knowledge of the deactivation mechanism of the parent compound [1], BODIPY derivatives that can both increase the ultrafast internal conversion to the electronic ground state have been synthetized [2] and investigated using quantum chemical calculations and non-adiabatic dynamics. Temoporfin is a commercialized photosensitizer for which an improved delivery formulation has been developed to enhance bioavailability, cellular uptake and selectivity. Using all-atom molecular dynamics simulations we provide a novel insight into the nature and the strength of the inter-molecular interactions between the drug and the carrier material, that are responsible for the carrier loading capacity and the drug-release mechanism [3]. In a second step, we have analyzed the effect of the surrounding hydrophobic environment on the relevant electronic excited states of Temoporfin.

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Conceptual vs. Computational Approaches to Energy Materials

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Increasing the energy density of cathode materials is a central goal of the ongoing research in Li-ion batteries. This implies improving simultaneously the capacity and the potential of the ma- terials used at the positive electrode of the electrochemical device. Today, the amplitude of the electrochemical potential of an electrode material is relatively well-controlled through an appropriate choice of the redox centre involved in the Li-driven electrochemical reactions.[1,2] Meanwhile, increasing the capacity of high-potential materials is more difficult to achieve without penalizing the material structural stability. So far, materials showing the highest energy densities are the Li-rich layered transition metal oxides for which a cumulative cationic and anionic redox activity has been demonstrated.[3-6] Nevertheless, the origin of extra-capacity in these systems has raised controversial debates in the literature with no real consensus about the directions to follow to overcome the structural instability that often comes along with the anionic process.[7-9] In this presentation, we use simple concepts of chemical bonding, band structure theory and topological tools of the electron density to address the fundamental question of high-energy-density of current batterires with the hope that a common language will help in clarifying the relationship between the material electronic structure, the potential, the (extra)-capacity and their consequence on the material structural stability. [10] This unified picture clearly highlights the trade-off that needs to be found between potential and capacity for the next generation of Li/Na-ion batteries.

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Quantum Mechanochemistry: Lightening up the Force

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Quantum mechanochemistry [1] comprises the theoretical description of mechanochemical processes by quantum chemical methods. In this talk, the JEDI approach to analyse the distribution of mechanically exerted energy in molecules is presented, which allows for the prediction of the force-bearing scaffold based on quantum chemical calculations alone. Also, the *in silico* development of a molecular force probe for spectroscopic monitoring of forces acting during protein folding is shown.

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On the Mechanism of Bistability in DTA-based Molecular Magnets

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Theoretical predictions of magnetic properties of bistable purely organic molecule-based magnets have experienced an incredible progress during the last years. Our attention is focused on dithiazolyl (DTA)[1,2] compounds, being promising candidates for potential technological applications (e.g. storage devices, quantum computers, etc.). Here, we identify the magnetic topology of the molecular crystals,[3] and we assess whether structural as well as electronic factors affect the magnitude of the overall radical···radical J_{AB} magnetic coupling. We provide magneto-structural correlation maps as a function of the substituents of the DTA-moiety to highlight which is the static ferromagnetic fingerprint region[4]. Moreover, a new mechanism for inducing spin transitions in materials based on planar organic radicals has been uncovered by means of a combination of static and dynamical analysis. The corresponding results and conclusions will be presented.

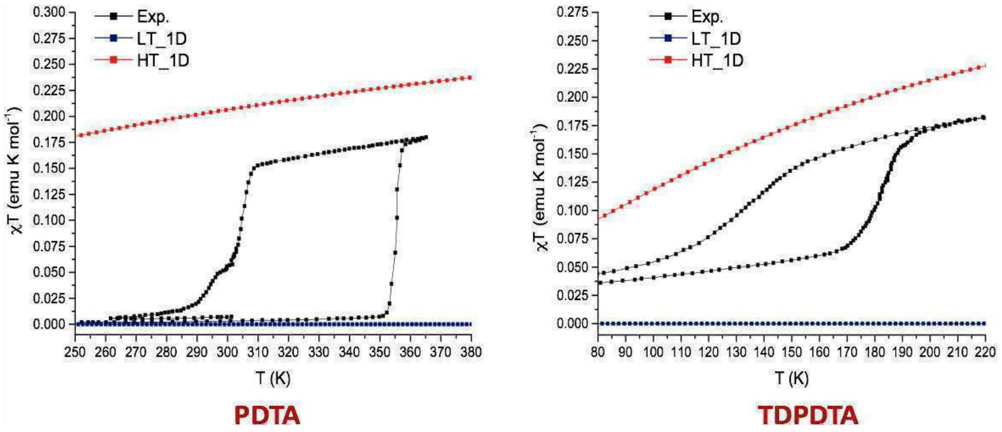

Figure 1. Comparison between experimental (■) and computed (🟥/🟦) susceptibility curves for the low temperature (LT) and high temperature (HT) phases of PDTA and TDPDTA systems. In particular, here the reported the results for the best 1D models for both the polymorphs considered in both materials.

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Manipulating azobenzene photoisomerization through strong light-molecule coupling

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The formation of hybrid light-molecule states (polaritons) offers a new strategy to manipulate the photochemistry of molecules[1]. Polaritonic states are formed when the coherent energy exchange between the molecule and a confined mode of the electromagnetic field is faster than any decay rate of the light-molecule system[2]. The confinement of the field to enter the strong coupling regime has been achieved experimentally by encapsulating a molecule into optical or plasmonic nanocavities[3]. In this work, we resort to a FOMO-CI[4] based approach to investigate the influence of the strong coupling on the azobenzene excited states.

Traditionally, a balance between computational performance and accuracy in the study of photochemical processes relies on non-adiabatic dynamics techniques in the semiclassical framework (Surface hopping algorithms)[5]. By reworking one of such techniques to take into account the hybrid light-matter nature of polaritonic states, we investigate the photochemistry on polaritonic states of azobenzene in vacuum[6]. At last, we present the results of the photochemistry in a more realistic system under the strong coupling regime. To this aim, we include the environment by mimicking recent successful experimental setups[3] through a QM/MM approach.

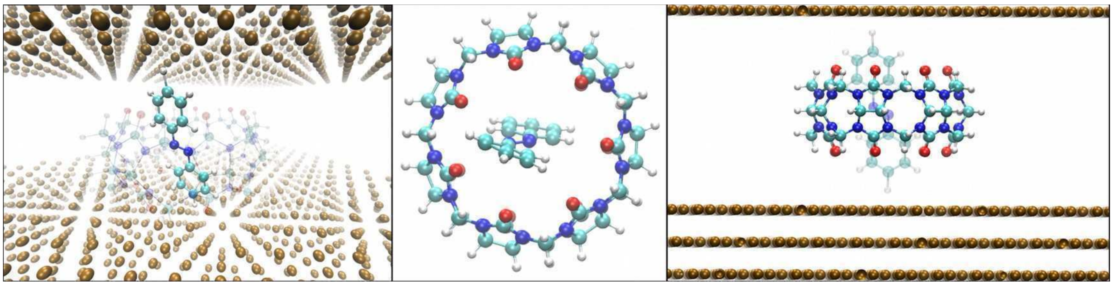

Figure 1. Azobenzene encapsulated into cucurbit-7-uril and two Au layers. The setup of the system allows to achieve the strong coupling regime for azobenzene.

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A General Route to Include Pauli Repulsion and Quantum Dispersion Effects in QM/MM Approaches

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Modeling the effects of the surrounding environment on a probe chromophore is still an open research topic in theoretical chemistry. In fact, the response and the optical properties of a molecular system can vary dramatically depending on the structural and electronic properties of the surrounding environment [1]. To adequately account for such effects at a reasonable computational cost, the most general and successful approach is to resort to focused models, where the chromophore is described at the Quantum Mechanical (QM) level, whereas the environment is treated classically, through ad-hoc optimized force fields defined within a Molecular Mechanics (MM) framework [2]. The most reliable QM/MM methods belong to the so-called polarizable QM/MM family, where the mutual polarization between the QM and the MM portions of the system is introduced [3]. Most of QM/MM approaches focus on modelling electrostatic interactions, whereas non-electrostatic interactions are only considered at a purely classical level, for instance by exploiting the Lennard-Jones potential, i.e. completely independent of the QM density.

In this contribution, a model to include Pauli repulsion and dispersion interactions formulated in terms of the electron density is presented and discussed [4]. In particular, the Pauli Repulsion term is written as a two-electron involving the QM density and a fictitious s-type Gaussian distribution placed on the MM region [5]. The dispersion term is instead formulated by generalizing the Tkatchenko-Scheffler approach originally formulated for dispersion corrected DFT functionals [6,7]. The performances of our model will be discussed, as well as the comparison between QM/MM and full QM calculations, for selected test applications.

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Drug Metabolites Theoretical Collision Cross Section Calculation and Chemical Dynamics Simulations for Their Collision-Induced Dissociation

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Ion Mobility Mass Spectrometry (IM/MS) is a technique that allows separation of isomeric species based on differences in their gas-phase collision cross sections (CCSs), thus providing specific information on the potential structure of a compound [1]. Along with Molecular Modelling, it is a potential tool for small molecule identification by measuring their gas-phase CCSs and comparing them to theoretically derived CCS databases. A protocol for theoretical determination of CCS has been introduced in [2] and its improvement is in progress. Our group has developed a script – an extensive automation of the protocol, which allows all the routines and necessary steps of the algorithm to be performed automatically. Furthermore, new atomic parameters employed in the CCS determination software (MOBCAL [3]) have been introduced: the protocol has been modified to be able to distinguish between different atom types and to assign appropriate parameters. Broad tests of the protocol with the featured parameters have been made to assess the performance of the new script. The results have shown that there is a systematic inconsistency with the experimental data that must be studied further.

A possible source for the observed discrepancy may be the fact that experiments were run in the environment filled with Nitrogen gas, whereas theoretical calculations were performed in Helium. Even though a correction factor has been introduced to tackle the issue, a reparameterization of MOBCAL to calculate metabolites' CCSs assuming atoms interacting with Nitrogen gas has been considered as a better workaround. That required a calculation of new Lennard-Jones parameters for "atom type - N2" pairs and their implementation in the software. Additionally, chemical dynamics simulations for collision-induced dissociation of molecules under study are in course with the aim of getting more information about the fragmentation process. Theoretical identification of fragmentation pathways may contribute to a better understanding of the processes in the MS part [4]. Such simulations are performed with the software packages VENUS [5] coupled to MOPAC [6] for electronic structure calculations.

Thus, further research is aimed at investigating deeper the influence of the introduced changes as well as searching for possible sources responsible for the differences between the theoretical and experimental CCS values considering newly obtained results.

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Non-radiative decay paths in organic π-conjugated compounds of interest in optoelectronics: A TDDFT and CASSCF/CASPT2 study

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In the framework of organic optoelectronics the luminescence properties of distyrylbenzene cyano functionalized type molecules, namely DSC molecules, are studied (see Figure 1). The nonradiative deactivation paths of DCS molecules are primarily explored by using the time dependent density functional theory (TDDFT) followed by a deeper analysis with the complete active space self-consistent field method (CASSCF) in combination with the complete active space second order perturbation theory (CASPT2). For comparison, the absorption, emission and conical intersections (CIs) of simpler but chemically similar molecules such as ethene, styrene and bistyrene, are also studied, together with the related spectroscopic features of other molecules of interest in the field (indoline [1] and fluoren-9-ylidene malononitrile [2]). Both TDDFT and CASSCF/CASPT2 methodologies lead to absorption and emission properties in line with experiments. A rough TDDFT exploration of the CI region in α and β cyano functionalized DCS molecules as reported by Shi et al [3] gives the hint for the main geometrical parameter that might be involved to reach such CI regions (twisting of the non-cyclic double bond). Besides, energy profiles along distortions of the vynil double bond at CASSCF/CASPT2 level stress out the actual influence of cyano groups in the accessibility of the CI region.

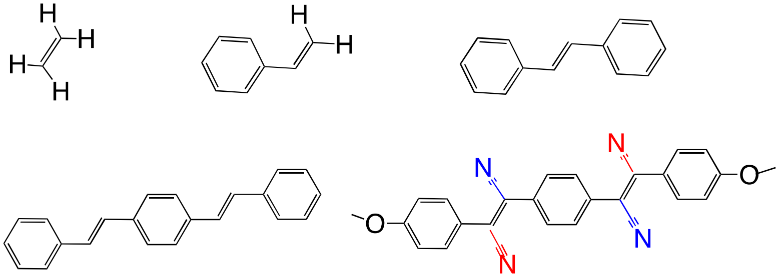

Figure 1. Chemical structure of molecules under study. From left to right, ethene, styrene, bi-styrene, DSB α or β DMDCS molecules.

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Using BSE/*GW* theory for organic compounds: successes and limits

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Time-Dependent Density Functional Theory (TD-DFT) is the most widely used method to model electronically excited-states [1]. However, as its wavefunction alternatives, it suffers from a specific limitations. As a consequence, other methods able to reproduce excited-state properties at a moderate computational cost are always welcome. Among those approaches, the Bethe-Salpeter (BSE) scheme, an extension of the ground-state *GW* method, offers an appealing alternative to TD-DFT, as it maintains the same scaling with system size [2]. In this talk, the performances of BSE/*GW* for excitations energies of molecules will be presented, considering vertical transitions [3], 0-0 energies [4] and oscillator strengths [5]. It will be shown that a partial self-consistent scheme at the *GW* level leads to a significantly reduced dependency on the starting DFT functional compared to both TD-DFT and BSE/G_0W_0 [3,6], as well as an accuracy similar to the one of reference wavefunction approaches for singlet [6] but not for triplet [7] states. Finally, applications on large systems [8] as well as inclusion of solvent effects [9] will be discussed.

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Application of a Pharmacophore-Enhanced Consensus Docking Approach for the Identification of STARD3 Inhibitors

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STARD3 is a cholesterol-specific START protein located in the late endosome membranes and involved in the cholesterol homeostasis. It regulates the first step in lipid steroidogenesis controlling the mobilization of cholesterol from the membranes in response to hormone stimuli [1]. STARD3 has been found to be overexpressed in about 25% of breast cancer with prevalence for malignant compared to benign tumours. Therefore, the inhibition of this protein could represent a new strategy to fight tumours growth and spread [2].

The crystal structure of STARD3 has been solved in the *apo* form. The three-dimensional organization of the binding pocket clearly showed that the hydrophobic tunnel is wide enough to accommodate only one molecule of cholesterol [3]. Nevertheless, clear data about the binding mode of cholesterol are still missing.

As a first step in this work, we analysed how cholesterol could interact with the protein binding site. An in-depth docking evaluation based on a *consensus docking* approach [4] was applied to dock cholesterol and allowed us to predict a reliable binding mode for the molecule into the STARD3 binding site.

Based on the key cholesterol-protein interaction identified by the docking calculations, we set up a STARD3-tuned virtual screening (VS) protocol, which was used to screen a commercial dataset of compounds. A five features structure-based pharmacophore model was developed and applied as first filter in the screening protocol. Then, a *consensus docking* approach followed by molecular dynamic (MD) simulations was employed to refine the screening.

As a result, four hit compounds were purchased and subjected to inhibition assays. A pyrimidine derivative, compound VS1, showed an interesting activity, thus representing the first reported STARD3 inhibitor.

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Networked computing for ab-initio modeling the chemical storage of renewable energy

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The Density Functional Tight Binding (DFTB) method and its evolution Self Consistent Charge DFTB (SCC-DFTB) have proven to be efficient methods in order to deal with extensive potential energy calculations when simulating the molecular dynamics, Monte Carlo or global optimization procedures of large systems.

The electronic bonding and structural organization of transition metals an in particular ruthenium requires an adequate description of both delocalized and atom-localized electrons, as well as the mixing between the d and s atomic shells. In order to account for the balance between electronic delocalization and electronic spin coupling, we have complemented the DFTB-SCC scheme with an explicit atom-localized spin term. We intend to investigate the ability of DFTB to provide reliable results about electronic structure, structural properties and stability of monometallic ruthenium systems covering the size range from small clusters to larger nanoparticles and the bulk.

The work presents the benchmark of the method by analyzing Ru_N clusters (N from 3 to 20) for several charge cases, namely neutrals, cations an anions. Simple cubic structures with pentagonal patterns are often obtained as representative building blocks as seen previously from other works [J. Phys. Chem. B 2004, 108, 2140-2147]. The binding energies per atom obtained fall inside the range of the accuracy of DFT calculations reported from other works. Ionization potentials and electron affinities are derived as well (both vertical and adiabatic).

We show that SCC-DFTB is in general agreement with DFT and available experiments in the small-medium size regime regarding the energetic ordering of the different low-energy isomers and simultaneously allows for an overall satisfactory yield of bulk properties. A consistent convergence between the cohesive energies of the largest investigated nanoparticles and the bulk's is obtained. On the basis of our results for nanoparticles of increasing size, a two parameter analytical extrapolation of the cohesive energy is proposed. This formula takes into account the reduction of the cohesive energy for undercoordinated surface sites and converges properly to the bulk cohesive energy. Values for the surface sites cohesive energies are proposed.

The effect of ball-milling on crystallinity, polymerization degree and thermal behavior of cellulose: a systematic study

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The increasing interest in biomass as a renewable resource to produce biofuels and value-added chemicals is followed by the need to understand how the different properties of biomass can affect its behaviour. Cellulose is the most abundant polymer on Earth, and the main component of biomass. The physico-chemical properties of cellulose are greatly influenced by two parameters: the crystallinity index (CI) and the degree of polymerisation (DP). These parameters are known to affect the thermal stability, water-binding ability, mechanical properties and reactivity of cellulose [1,2]. A widely used technique to regulate the CI of cellulose is ball-milling. However, there is little to no data about the effect of ball-milling on the other properties of cellulose.

In this study, four different reference cellulose samples were milled at different times, and the effects of milling on CI, DP, thermal stability and reactivity were determined with multiple analytical techniques. CI was determined with X-ray diffraction, and DP was measured with Size-Exclusion Chromatography.

Thermal stability was evaluated using evolved gas analysis-mass spectrometry (EGA-MS), which provides fundamental data on the thermal stability and the reaction kinetics. EGA-MS has been widely applied to the study of cellulose. It has been recently proved that isoconversional methods, usually applied to TGA data, can also be applied to EGA-MS data [3]. For this reason, isoconversional methods were used to estimate the activation energy for cellulose pyrolysis.

Finally, the reactivity of cellulose in a pyrolytic environment was tested using analytical pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC/MS). This is another powerful technique which provides detailed compositional data on the pyrolysate. The performance of a Py-GC/MS analysis can be enhanced using in situ derivatisation, which increases the range of detectable compounds [4]. Reactive pyrolysis can be used to overcome partial derivatisation and reduce the chromatograms complexity, by keeping the sample at elevated temperature and pressure for long times [5]. Reactive Py-GC/MS experiments were performed using in situ derivatisation with hexamethyldisilazane (HMDS).

This work provides a starting point for the systematic rationalisation of the effect of milling on CI, DP, thermal stability and reactivity of cellulose.

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Computational strategies for the calculation of accurate molecular structures

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The knowledge of the equilibrium structures of isolated molecular systems of chemical and biological interest is of fundamental relevance to gain detailed information on many chemical-physical processes, in the framework of the so-called structure-property relationships. Moreover, accurate equilibrium geometries serve as benchmarks in the development of new computational strategies. Molecular structures obtained through isotopic substitution are subject to vibrational average, and then strongly depend on the isotopic species under investigation. In this respect, the determination of the equilibrium structure, i.e. the geometry associated with the Born-Oppenheimer (B-O) potential energy surface minimum, is the most appealing alternative [1]. While this type of structure is more challenging to be inferred at the experimental level, its determination allows the inclusion of vibrational effects and, within the B-O approximation, it is isotopic substitution independent. Furthermore, such structures are directly comparable with theoretical results. In this contribution we present the new program MSR (Molecular Structure Refinement) [2], specifically devised for computing equilibrium structures by means of the semi-experimental approach [3,4]. The program includes a large panel of optimization algorithms and an extended error analysis [5]. Particular attention has been devoted to the definition of the internal coordinates to be employed in the refinement. The approach developed in this framework, which is particularly advantageous when symmetric molecules are studied, is implemented as a completely automatic black-box procedure. The MSR program is also equipped with the possibility of including predicate observations in the fit [6]. By means of this method, the set of input data (i.e. the rotational constants of different isotopologues) can be augmented by estimates of structural parameters obtained, for example, through quantum-chemical calculations. In this contribution, the underlying theory and the organization of our implementation are presented in some detail. The reliability of the code is proven by applications of A_1 coordinates and predicate observations to the determination of the equilibrium structure of medium-size organic and biological molecules.

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Surface hopping within an exciton picture – An electrostatic embedding scheme

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Electronic excitation energy transfer (EET) is the fundamental process observed in biosystems and materials through which an excited chromophoric unit (the donor) nonradiatively transfers the excitation energy to another proximate unit (the acceptor). One of the most prominent examples of this process is the initial step of photosynthesis, where the excitation energy is transferred many times in and between pigment-protein complexes until the reaction center is reached. [1, 2]

The theoretical investigation of EET processes can be highly challenging due to (i) the size of the involved system, (ii) the influence of the environment and (iii) the complexity of the involved dynamics. [3]

To address these problems we developed an hybrid QM/MM exciton scheme with mechanical and electrostatic embedding for non-adiabatic molecular dynamics. Hereby we utilize the Gaussian 09 suite of codes for the electronic structure calculation and combine it with the SHARC (Surface Hopping Including arbitrary couplings) scheme [5, 6] for the surface hopping dynamics.

We apply our approach to a molecular dyad consistent of a BODIPY moiety covalently bonded to a tetrathiophene group. The results using our exciton Hamiltonian were compared with those obtained on the whole system treated at TDDFT level of theory. [4] Although covalent linked systems represent quite challenging cases for simple Frenkel exciton models, the obtained results show an excellent agreement with the full TDDFT. [7]

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Theoretical modeling of materials and processes in dye-sensitized solar energy conversion devices

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In the context of solar energy exploitation, dye-sensitized solar cells (DSCs)[1] and dye-sensitized photoelectrosynthetic cells (DSPECs)[2] offer the promise of cost effective sunlight conversion and storage, respectively. Dye-functionalization of bot n- and p-type semiconductors (like TiO_2 and NiO, respectively) can be either exploited to build active DS photoelectrodes or tandem DSC and DSPECs devices (Figure 1). Computational modelling has played a prominent role in the development of the DSC technology, whereas the understanding of the interfacial processes in DSPEC is still at its inception. Here I will discuss the recent advances concerning first principle modelling of materials (chromophores, catalysts and semiconductors), interfaces and processes of active photoelectrodes for solar energy and solar water splitting.[3] Particular emphasis will be devoted to the role of the solvent on electronic and optical properties of the isolated cell components as well as of the interfaces. I will present the characterization of the electronic and structural properties of the complex NiO/solvent/dye/interface, whose investigation is still poor when compared to the level of understanding reached for TiO_2 sensitized photoanodes, from both the experimental and computational point of view. I will discuss the main methodological limitations of state-of-the art DFT methodologies in predicting the energy level alignment across the dye/semiconductor interface and the challenging definition of a proper structural model needed to reliably capture the interface complexity.[4]

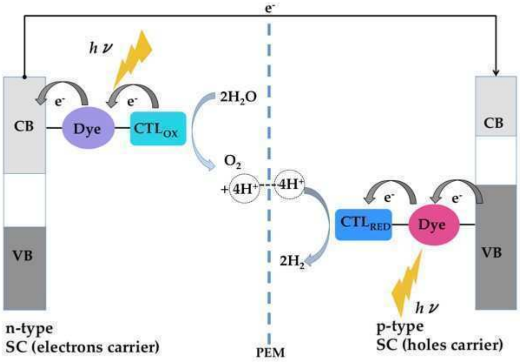

Figure 1. Scheme of a DSPEC

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Time-dependent correlation function approaches to molecular spectroscopies

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Time-dependent correlation function approaches to molecular spectroscopies are computationally efficient alternatives to time-independent, Golden-Rule or Kramers-Heisenberg-Dirac type methods. By directly correlating spectroscopy with dynamics, they are also useful for interpretative purposes. In these approaches, the spectroscopic signal is typically expressed as a Fourier transform of a quantity C(t), which is either a quantum mechanical correlation function obtained from wavepacket propagation, or a classical correlation function obtained from an (ensemble) average over classical trajectories.

In the talk, I will present some of our contributions to the field. First, recent work on vibrationally resolved spectra involving electronically excited transitions (UV/vis absorption and emission, resonance Raman and photoelectron spectra) of medium-sized, organic molecules will be reviewed [1,2,3]. Here, *quantum* correlation (and cross-correlation) functions were computed in the harmonic approximation. Extensions to treat non-radiative transitions, anharmonicity and dissipation [4] will also be presented. We then move on to *classical* auto- and cross-correlation functions, which are used for linear (IR) and non-linear (VSF, Vibrational Sum Frequency) vibrational spectroscopies of adsorbates at surfaces, namely water molecules on a (hydroxylated) alumina substrate [5].

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Predictive Kinetics in Organometallic Catalysis

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Computational chemistry may provide an important insight into the field of catalysis. In sustainable catalyst design it is crucial to understand the mechanism of catalytic reaction and accurately locate the bottleneck(s) of the process: selectivity and rate determining step(s). Theoretical methods may provide an important contribution to these studies by exploration of Potential Energy Surface of the investigated system and resolving the mechanism of the reaction by application of quantum chemistry theories. The huge development of *ab initio* methods and computational tools in the last decades enabled scientists to study *in silica* catalytic reactions of biological and industrial significance. In our group we have shown that a computational protocol consisting of density functional theory and coupled cluster singles and doubles with perturbative triples calculations together with transition state theory may enable to quite accurately predict the experimentally measured rates of the industrially important propene hydroformylation by cobalt catalyst [1]. In a follow-up research the selectivity and temperature dependence of the reaction is addressed as well.

Yet another goal of computational chemistry would be to foresee the plausible catalytic reactions that could be experimentally applicable. One of such reactions would be the direct functionalization of abundant methane to higher value chemical commodities [2]. Based on the latest evidence that small ring-like aluminium oxide cluster radicals could activate methane [3], we have explored whether similar compounds, alternant N_2Y_2 (Y = O, S) rings investigated previously in our group [4], may be capable of reacting with methane too.

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SHARC Photodynamics of the *trans*-$[RuCl(NO)Py_4]^{2+}$

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Ruthenium nitrosyl complexes have found utility in a variety of applications, such as optical switches, data storage, and medicine. Depending on the ancillary ligands, environment, and irradiation wavelength, these complexes can undergo either intramolecular NO linkage photoisomerization or NO photorelease (Figure 1). In the past years, DFT studies of both the NO linkage photoisomerization and photorelease process in the trans-$[RuCl(NO)(py)_4]^{2+}$complex revealed a complex two-step photoisomerization mechanism involving a sequential two-photon absorption.[1,2] This mechanistic picture has been confirmed experimentally recently.[3] The DFT study was based on the exploration of the lowest singlet and triplet potential energy surfaces, assuming efficient decay via intersystem crossing (ISC) from the first singlet excited state to the lowest triplet state. A further ab initio CASSCF/CASPT2 study[4] has supported and completed the DFT and experimental findings. In particular, the spin-orbit coupling outcomes helped to uncover the first steps of the photoisomerization process, suggesting an efficient singlet to triplet intersystem crossing after light absorption. At the same time, the topology of the CASPT2 potential energy surfaces highlighted the possibility of several photoisomerization pathways. It would be desirable to verify these hypotheses, by determining the most probable pathways. In this context, the surface hopping dynamics including arbitrary couplings (SHARC) method[5] represent a useful analytic tool to better understand the photochemistry of this system. Thus, in my presentation, I will present the results of the full dimensional surface hopping SHARC dynamics on the trans-$[RuPy_4ClNO]^{2+}$ including non adiabatic and spin-orbit couplings, that describe: i) the role of the singlet and triplet excited states ii) the branching ratio between the different photoisomerization pathways iii) the most important quenching funnels that slow down the entire N→O isomerization process.

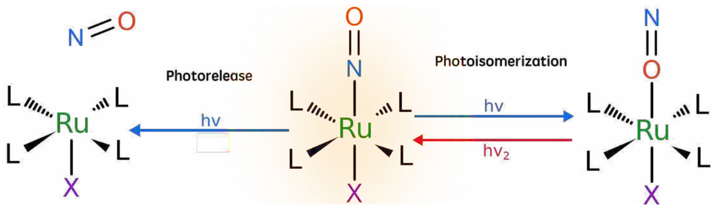

Figure 1. Photoisomerization and photorelease processes of a ruthenium nitrosyl complex

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Gas adsorption on graphene: Introducing flexibility in the graphene sheet

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Graphene and derived products have shown great promise in the context of gas adsorption, possible applications range from environmental protection over gas sensing to energy storage. An important issue in the understanding of the involved principles, will be the movement of graphene itself. We have performed molecular dynamics calculations on the adsorption of different gases like methane, hydrogen, nitrogen, water and carbon monoxide including an intramolecular force field for graphene [1]. More specifically we have used and compared three different force fields found in the literature [2][3][4], one of which was originally developed for carbon nanotubes, while the other two were constructed specifically for graphene. Two of the force fields include stretch, bending and torsional terms, while the third one only uses stretch and bending terms. We have thus compared the behavior of a flexible graphene sheet to a more conventionally used rigid gaphene sheet within the context of gas adsorption.

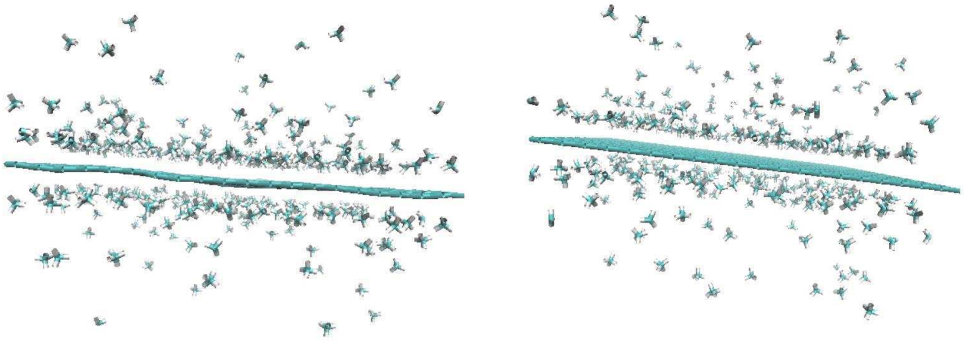

Figure 1. Adsorption of methane on a rigid (left) and flexible (right) graphene sheet.

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Nonadiabatic dynamics simulations for understanding the singlet fission mechanism in thienoquinoidal molecule

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Singlet fission (SF) is an ultrafast process whereby a photogenerated excited singlet state transfers part of its energy to a neighbouring ground state chromophore to form singlet coupled triplet pairs, $S_1 + S_0 \rightarrow {}^1TT$ [1]. This process can help to surpass the Shockley-Queisser limit of organic solar cells [2] because it exploits a high-energy photon to generate multiple charge carriers capable for charge separation. For an efficient SF process, the energetic condition of $E(T_2) > E(S_1) > 2E(T_1)$ for SF chromophores has to be met, as, for instance, in some alternant hydrocarbons and biradicaloids [1]. The excited state dynamics simulations of (at least) a pair of SF chromophores in molecular crystals or in covalently linked dimers permit to unravel the mechanism and to calculate the efficiency of SF. Here, we present the excited state dynamics simulations of a pair of thienoquinoidal molecules, namely 2,5-bis(fluorene-9-ylidene)-2,5-dihydrothiophene (ThBF) [3] embedded in its molecular crystal (Figure 1). We employed the surface hopping approach with quantum decoherence corrections [4]. In this approach, the electronic wave functions and energies are computed "on the fly" based on the semiempirical FOMO–CI method in its QM/MM version [5]. The results show that, 2 ps after the excitation, the most populated state is ${}^1TT$ and very little decay to the ground state occurs. We also find that the role of spin-orbit coupling is not negligible.

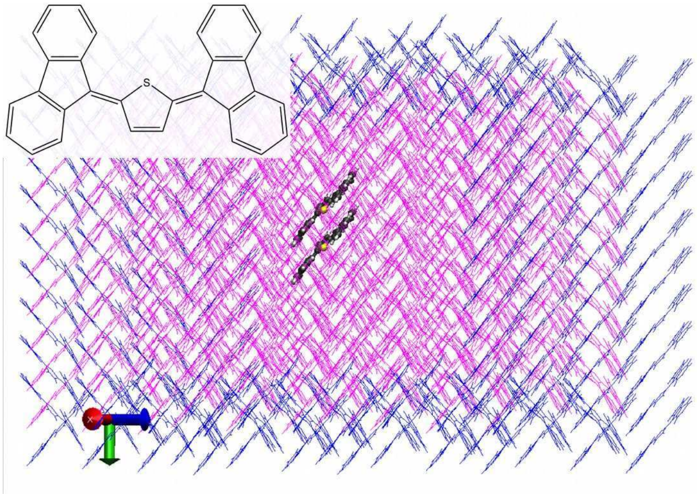

Figure 1. The crystal structure of 2,5-bis(fluorene-9-ylidene)-2,5-dihydrothiophene (ThBF).

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Poster presentations

Author	Title
Neus Aguilera-Porta	Computational approach on light influence on drugs photostability
Stefano Battaglia	Azide anion confined inside carbon nanotubes: quantum chemical study and molecular dynamics potential
Andi Cuko	Predicting the stability of small TiO_2 nanoparticles with an artificial neural network
Gabriele Dalla Torre	Aluminium: a mysterious ion
Giovanna D'Angelo	Collision induced reactions of 5-bromouracil hydrated clusters
Martina De Vetta	Liposomal assisted delivery of the temoporfin photosensitizer: insight from molecular dynamics simulations
Tommaso Francese	On the mechanism of bistability in molecular magnets
Dymtro Ivashchenko	Drug metabolites theoretical collision cross section calculation and chemical dynamics simulations for their collision-induced dissociation
María Izquierdo	Computational modelling of excited state processes in optoelectronic materials
Carles Martí	Networked computing for ab-initio modeling the chemical storage of renewable energy
Maximilian F. S. J. Menger	Surface hopping within an exciton picture – An electrostatic embedding scheme
Ewa Szlapa	Predictive methane activation by alternant N_2Y_2 ($Y = O, S$) ring cations
Ewa Szlapa	Activity and selectivity of cobalt catalyst in hydroformylation of propene
Francesco Talotta	Ab initio investigation of the NO photorelease in the ruthenium nitrosyl complex trans-$[RuCl(NO)(py)_4]^{+2}$
Jelle Vekeman	Gas adsorption on graphene: Introducing flexibility in the graphene sheet
Meilani Wibowo	Resolving the singlet fission dynamics at QM/MM level