

11th Symposium on Computing π -conjugated Compounds

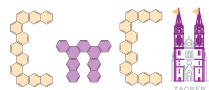
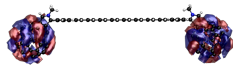
Book of Abstracts

Division of Theoretical Physics and Division of Physical Chemistry
Ruđer Bošković Institute, Zagreb, Croatia



30th January - 1st February 2020

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Foreword

Dear Friends and Colleagues,

we are pleased to welcome you to the *11th Symposium on Computing π -conjugated Compounds (C π C11)* on Friday 31 January - Saturday 1 February 2020, hosted by the Ruđer Bošković Institute in Zagreb. Since 2010, C π C is a yearly convivial meeting of European scientists working on π -conjugated molecular systems. The symposium is an opportunity to address recent developments in theory and methods and discuss computational results that have helped to unravel the complex behaviour of π -conjugated compounds.

In the spirit of C π C short / small / cheap / local / open / young

Luca Grisanti, Ivor Lončarić, Ivan Ljubić and Aurora Ponzi

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Invited oral presentations

Molecular dynamics simulation of water on graphene

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Simulations of molecular dynamics were performed for water box with dimensions $30 \times 30 \times 80$ Å on a graphene surface. Cartesian coordinate space was sampled using *on-the-fly* calculations of forces in every point of the simulation. Parallel localized type of molecular dynamics was used for calculation of trajectories where each point in simulation was divided into a batch of local calculation consisting of n molecules for which the forces are calculated (inner system) and all molecules within 5 Å distance for molecules that serve as a local external potential (outer system). All local calculation were computed simultaneously using the parallelization algorithm that sends each local calculation to a separate processor core(s). Molecular dynamics simulations were performed using our own program *qcc*^{1,2} and calling the external program for quantum chemical computation.

Probability distribution function for water molecules in dependence on the distance from the surface was calculated and compared to other types of surfaces. Water distribution were analyzed by means of local maxima position, total number of water molecules in the extrema points and overall shape of the probability distribution function. Local maxima represent the increased density water layers characterized by the total number of counted water molecules, whereas the asymptotic behaviour of probability density functions reveals position of the bulk water.

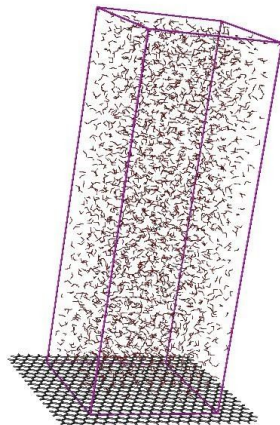


Figure 1. Water box ($30 \times 30 \times 80$ Å) placed on a graphene.

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Excited State Dynamics of β -Carotene Revealed Utilizing Ultrafast Laser Spectroscopy

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Carotenoids play an important role in photosynthetic systems, acting as light-harvesting pigments that absorb the sunlight and transfer the energy of light to photosynthetic reaction centers. Determination of the excited-state dynamics of carotenoids has attracted considerable interest, engendering a number of controversial hypotheses because of the strongly overlapping spectral peaks and complicated dynamics of transient species. Andersson and Gillbro¹ provided first picture of relaxation pathways in carotenoids based on the well-known three states scheme. In order to explain the results obtained in various ultrafast spectroscopy studies, additional states lying between the S_1 and S_2 states were proposed: the so-called "dark excited states". One of the key arguments for the proposal of additional states came from the observed anomalous N-dependence (N being number of conjugated double bonds) of the S_2 - S_1 internal conversion rate. It was observed that, while the S_2 - S_1 energy gap increases with conjugation length, the S_2 lifetime decreases for longer carotenoids².

In this talk I will present results of femtosecond pump-probe study of excited-state dynamics of all-trans- β -carotene³. Following an excitation of the strongly allowed S_2 state of the β -carotene, transient absorption spectra were recorded in the visible spectral range. Conventional analysis of time-resolved transient absorption spectra is complemented with advanced methods: soft-modeling multivariate curve resolution alternating least-squares analysis (MCR-ALS) method for modeling pure profiles and the generalized two-dimensional (2D) correlation spectroscopy data analysis for providing additional information on the dynamics of spectral features. The soft-modeling MCR-ALS method is a model-free mathematical method for recovery of the concentration profiles and pure spectra of spectroscopically active species, based on the superposition of the spectroscopic properties principle arising from the Lambert-Beer law and a least-squares minimization. The method can describe reaction processes without explicitly using the underlying chemical model to which they are linked. Furthermore, two-dimensional (2D) correlation spectroscopy, which performs cross-correlation analysis of a series of spectra describing a system evolving along some external perturbation, is further used to describe the dynamics of spectral features, highlighting both correlated and uncorrelated spectral changes of excited-state dynamics of β -carotene. Conclusion drawn from the analysis indicate that the observed S^* state is not the hot S_{1v} state but instead a separate singlet state, a different conformational state of a S_1 state that could be formed by twisting of the carotenoid backbone.

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Ultrafast electronic excitations in π -conjugated compounds

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The coupling of electronic and nuclear motion is fundamental to the understanding of photoinduced processes. While accurate methods for the solution of the nuclear time-dependent Schrödinger equation on coupled electronic surfaces have been developed, the computational effort of such calculations is very high. This is why nonadiabatic molecular dynamics simulations have emerged as an important tool for studying photoinduced processes in complex systems.

Over the last few years, our group has used nonadiabatic dynamics simulations based on the surface hopping procedure to elucidate the mechanisms of radiationless excited-state deactivation of a variety of π -conjugated compounds. Specific examples include explanation of (i) the fluorescence quenching in tetraphenylethylene, a prototypical example of a molecule displaying aggregation-induced emission,¹ (ii) the very different excited state reactivity of 1- and 2-naphthols and their water clusters² and (iii) the excited state behaviour of nucleobases in aqueous solution.³

In this talk particular attention will be paid to the validation of dynamics results against benchmark electronic structure calculations and to the link with experiment.¹⁻³

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Contributed oral presentations

Hybrid materials for artificial photosynthesis

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In recent years, research effort has been devoted to the generation of hybrid materials which change the electronic properties of one constituent by changing the optoelectronic properties of the other one. The most appealing and commonly used approach to design such novel materials relies on combining organic materials or metals with biological systems like redox-active proteins. Such hybrid systems can be used e.g. as bio-sensors, bio-fuel cells, biohybrid photoelectrochemical cells and nanostructured photoelectronic devices. Although experimental efforts have already resulted in the generation of a number of hybrid bio-organic materials, the main bottleneck of this technology is the formation of a stable and efficient (in terms of electronic communication) interface between the biological and the organic/metal counterparts. In particular, the efficiency of the final devices is usually very low due to two main problems related to the interfacing of such different components: charge recombination at the interface and the high possibility of losing the function of the biological component, which leads to the inactivation of the entire device.

Here, we present a multiscale computational design which allows the study of complex interfaces for stable and highly efficient hybrid materials for biomimetic application, consisting of single layer graphene (SLG) as organic material/metal and light harvesting protein complex (Photosystem I) as biological counterpart, linked together via a self-assembly monolayer (SAM) and a biological linker (cytochrome c553) to allow flexibility of the whole system, in order to create novel biomimetic materials for solar-to-fuel, bio-transistors or bioorganic electronic applications. In particular, we focus on the SAM/SLG and cytochrome c553/SLG interfaces as models to validate our theoretical approach.¹⁻³

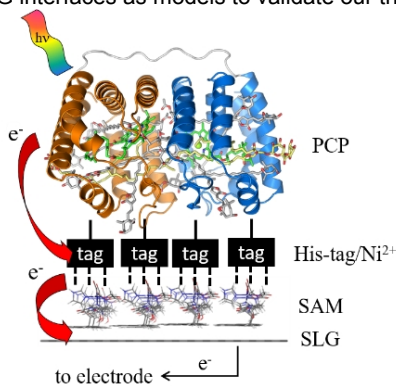


Figure 1. Rationally designed biohybrid architectures proposed from experiments.

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Anchoring of single-platinum-adatoms on graphene derivatives

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Noble-metal catalysts have been extensively exploited for industrial applications, including energy conversion, chemicals production, and automotive exhaust purification, just to name a few. Noble metals are, however, expensive and of limited supply. Catalytic reactions take place on metal surfaces and, therefore, metal atoms that are not accessible by the reactants are not involved in the catalysis and it is very beneficial to reduce amount of such inactive atoms. Dispersing ultra-small metal-particles onto high-surface-area supports, is an effective strategy to increase their usage efficiency and catalytic reactivity. The ultimate limit is an atomically dispersed catalyst, also termed single-atom catalyst (SAC), with nearly 100% metal dispersion making nearly every active site accessible. To prevent the undesirable aggregation of SACs compromising their catalytic reactivity, the metal catalysts should be anchored onto a high-surface-area support leaving a coordination sphere around SACs accessible for possible catalytic reactions. We identified that among graphene covalently functionalized by –OH, –F, –CN and –H, only –CN group was able to form stable complexes with Pt⁰/Pt²⁺ atoms/ions [1]. We synthesized cyanographene with 3.7 wt.% single Pt adatoms immobilized onto its surface. The effective immobilization on the cyanographene surface was also recently achieved for Cu and Fe ions [2].

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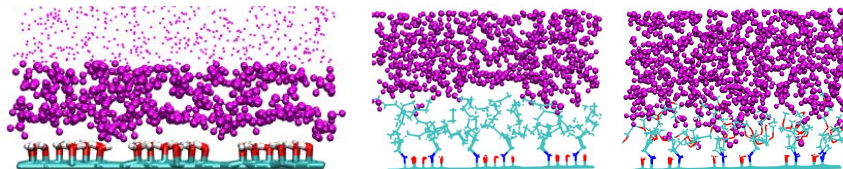
Graphene oxide and functionalized graphene oxide as humidity sensors

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Gas sensors based on two-dimensional (2D) materials are gaining significant scientific and industrial attention due to the selectivity, sensitivity, excellent conductivity, large specific surface area and ease of physisorption of the gas molecules on the 2D surfaces. Gas sensors with functional graphene, in its pristine and/or defective forms have shown high responsiveness and selective sensitivity to several small molecules, including water [1,3]. However, the defective nature of graphene combined with the selective sensitivity of small molecules to the defects [3], high cost of manufacturing and scalability hinders the development of efficient gas sensors based on pure graphene. Alternatively, graphene oxide (GO), graphene oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl groups) and composites of GO with polymer matrix such as PEDOT [4] or PEDOT:PSS [5] were proposed towards the development of low-cost, printable, flexible and sensitive gas and humidity sensors. Borini et al [6], proposed the development of fast (upto 30 ms of response and recovery times) and flexible humidity sensors based on GO layers. However, selective surface functionalization of these GO layers can further enhance the sensing capabilities as they offer wider selection of functional groups and higher specific surface area. In the present work, by combining experimental and theoretical studies, we demonstrate that the humidity response of GO can be further enhanced both in terms of its sensitivity and responsiveness by selective functionalization of the GO surface. To this end, the GO surface is functionalized with N,triethylene glycol aminomethyl ether (NTEG), and with decylamine, referred to as fGO and fGO1 respectively (Fig. 1), and their humidity response is characterized experimentally. Molecular Dynamics simulations were performed on GO and functionalized GO layers (fGO & fGO1) in water medium to assess the interaction strength of water with the respective moieties. The humidity response of fGO, principally driven by its interaction strength with water, is found to be significantly larger compared to that of GO and fGO1.



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From triangle-shaped radicaloids to molecular emitters for TADF-based OLEDs

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The light-emitting mechanism known as Thermally Activated Delayed Fluorescence (TADF), with its promise to achieve 100% of quantum efficiency in OLEDs, relies on an effective energy conversion between the lowest excited-states of different multiplicity (e.g. T_1 to S_1) followed by the corresponding fluorescence emission.¹ We propose here a new approach to the molecular design of active emitters², based on rigid (i.e. with reduced reorganization energies and thus narrower emission spectra with enhanced color purity) B- or N-doped triangle-shaped nanographenes (i.e. with multi-resonant charge-transfer effects leading thus to sufficiently small singlet-triplet energy difference without sacrificing moderate oscillator strength values), allowing to overcome some of the existing bottlenecks for the integration of this mechanism into next-generation operational devices.

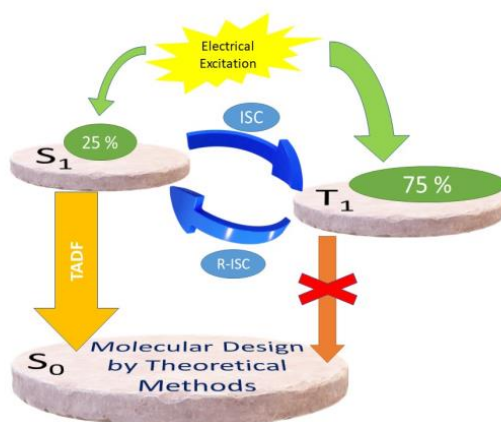


Figure 1. Sketch of the processes taking place for an effective TADF mechanism based on active conjugated organic emitters.

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Multiple Charge Transfer States in Donor–Acceptor Heterojunctions with Large Frontier Orbital Energy Offsets

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We have identified six donor-acceptor (D-A) systems that exhibit ~ 2 eV broad charge transfer (CT) state spectra, originating from the large optical gap of the D-A molecules and very low donor-HOMO acceptor-LUMO gap at the interface (i.e. very large frontier orbital energy offset). Being the exact opposite of the material systems recommended by the efficient organic photovoltaic design rules, these devices are expected to have severe non-radiative recombination loss and thus are ideal candidate to study loss mechanisms in-depth. To investigate the origin of the broad CT spectrum in detail, we have chosen an NPB:HAT-CN based bulk-heterojunction (BHJ) D-A system, which demonstrates three distinct sub-gap peaks in its external quantum efficiency (EQE) spectrum. We have performed comprehensive electrical and optical characterization, along with molecular dynamics and quantum chemical simulations to conclusively prove that the lowest two peaks in the EQE are indeed originating from distinct electronic CT state transitions. We have also found that the lowest energy CT state is non-emissive and acts as a significant non-radiative loss path, possibly due to the large vibrational overlap with the ground state, and as expected from the energy gap law of organic materials.

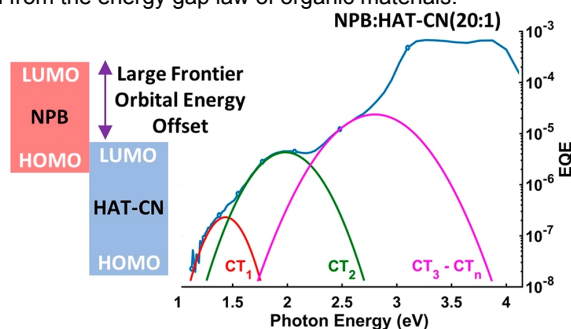


Figure 1: External quantum efficiency (EQE) spectrum of an NPB:HAT-CN (20:1; blue solid line) device.

Fused Quinoidal Oligothiophenes Imides with High Electrical Conductivity

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Organic diradicals are molecules containing two unpaired electrons, which are usually highly reactive.¹⁻² Although these organic diradicals present a wide range of potential applications, their air stability still remains as a major obstacle.³ In order to overcome this, new organic diradicals based on quinoidal oligothiophenes-derivatives (QOT) have been synthesized, *i.e.* BTICN, ISOCN and QTICN (see Figure 1). These new molecules present high stability and electrical conductivity, which have been achieved by employing imide-bridged fused molecular frameworks. The combination of strong electron-withdrawing imide with tetracyano groups in the conjugated skeletons also enabled extremely deeply aligned LUMO levels and large diradical character assisted by cross-conjugation.⁴ Here we use different experimental techniques and DFT calculations to provide new insights into the electron conduction mechanism of QOT diradicaloids, in order to demonstrate the great potential of fused quinoidal oligothiophene imides in developing stable organic diradicals and high-performance doping-free n-type conductive materials.

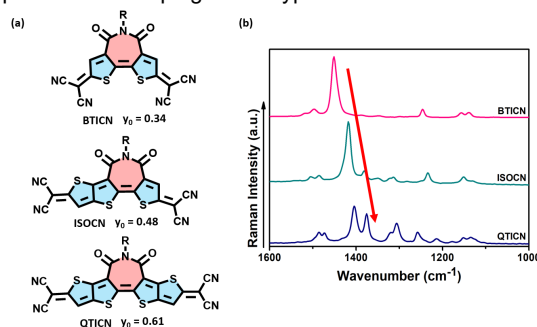


Figure 1. a) Chemical structures and b) FT-Raman spectra of quinoidal systems BTICN, ISOCN and QTICN studied in this work.

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Resilience to conformational fluctuations rather than planar backbones drives conjugated polymer materials with low-energy disorder. insights from atomistic simulations.

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The use of organic semiconductors in field-effect transistors has raised growing interest and efforts in the last decades, which led to outstanding improvements in their performances. It is now common to find organic conjugated materials with room-temperature charge carrier mobility exceeding $1\text{cm}^2/\text{Vs}$. Throughout the years, the highest values of the mobility were always reported for single crystals of organic small molecules. Increasing the crystallinity of conjugated polymer thin films in concert with the planarization of the conjugated backbones has therefore been considered as the key for success in the design of polymer materials with optimized charge transport properties. Recently, this general belief had to be revisited with the emergence of a new class of disordered or even seemingly amorphous donor-acceptor conjugated polymers that exhibit charge mobilities larger than $1\text{cm}^2/\text{Vs}$. In this contribution, we will review our recent theoretical works addressing the structural packing of working horse p and n-type conjugated polymer chains (PBTTT, NDITT, IDTBT, TIFBT, DPPs, ...) ¹⁻⁵ in the crystalline, disordered, and amorphous states by means of molecular dynamics simulations performed with properly parameterized force fields and the resulting electronic properties at a quantum-chemical level. Our results show that crystallinity of the materials and planarity of the polymer chains are not mandatory to get lowenergetic-disorder polymers that promote high charge mobilities. A key factor governing charge transport is the resilience of the equilibrium torsion angle between ordered and disordered phases whatever its absolute value, thus implying that twisted chains can efficiently transport charges. Whereas planar systems always promote efficient charge transport in crystalline domains, a dramatic drop of charge mobility is observed if the chains are no longer planar in disordered phases. Finally, we also demonstrated that the bulkiness of the monomer unit strongly modifies the nature of the intermolecular interactions between the chains and therefore plays a significant role in the resulting opto-electronic properties of films. ¹⁻³

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Theoretical study of Covalent Organic Frameworks based on C_3 -symmetric Central Cores

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In recent years, the design and synthesis of COFs (covalent organic frameworks) has been deeply investigated. These materials are constructed from the union of different covalently linked conjugated platforms and they have a wide range of analytical applications, such as adsorption and / or separation of certain compounds, catalysis or identification of analytes, among others.¹ On the other hand, the π -conjugated nature of these systems together with their extended 3D nature make them excellent candidates to be used in organic electronics.² Recently, in collaboration with the group of Dr. Berta G3mez-Lor, we have studied the electronic and optical properties of four new porous truxene-based polymers.³ The results of this work opens the door to the control of the degree of π -conjugation and therefore to the optoelectronic properties of these materials (*i.e.*, their potential as nitroaromatic compound sensors) through the substitution position of the truxene units. Here we propose to expand this study to COFs (Figure 1) derived from platforms with C_3 symmetry based not only on truxene ($X=C$) but also on triindole ($X=N$) and truxenone ($X=CO$) units by means of periodic DFT-calculations (see Figure 1). Specifically, we study how the different structural modifications affect the intra- and intermolecular properties of the systems for their subsequent synthesis and real application in organic electronic devices.

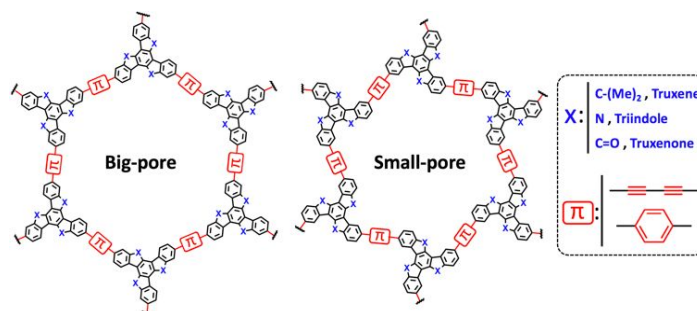


Figure 1. Chemical structure of COFs under study.

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Chasing the “Killer” Phonon Mode for the Rational Design of Low-Disorder, High-Mobility Molecular Semiconductors

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Charge transport in crystalline molecular semiconductors is intrinsically limited by the large-amplitude thermal molecular motion, which is a direct consequence of the weak van der Waals intermolecular interactions. This talk will present our recent modelling work dedicated to the understanding of the impact of molecular and lattice vibrations on the energetic disorder experienced by charge carriers and ultimately on the charge mobility.^{1,2,3} To such an aim, we developed a general protocol encompassing lattice dynamics calculations, electron-phonon models and charge transfer simulations based transient localization framework. Upon applying this strategy to a set of high-mobility ($\mu > 1 \text{ cm}^2/\text{Vs}$) molecular crystals, including rubrene, pentacene and thieno-acenes, we have been able to identify the long-axis sliding motion as a “killer” phonon mode, which in some molecules contributes more than 80% to the total thermal disorder.¹ Based on this insight, a way to rationalize mobility trends between different materials and derive important molecular design guidelines for new high-mobility molecular semiconductors is suggested.

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The Ad-MD|gVH method: computing electronic spectra of flexible molecules interacting with an environment

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Theoretical methods are pivotal to unravel the wealth of information retrieved by electronic spectroscopy, a ubiquitous tool in modern research. A current challenge for computational approaches is represented by flexible molecules in condensed phase, ranging from organic dyes in solution to larger molecular probes in heterogeneous systems. Even for the former simpler systems, a consistent strategy to retain the quantum mechanical (QM) nature of vibrational motion, while accounting for the effects of the environment on both the solute molecular structure and its electronic distribution, seems to be lacking. We propose a general mixed quantum classical method, which integrates vibronic models¹ and classical Molecular Dynamics (MD) simulations. The protocol is based on a partition of the nuclear motions of the whole system in "stiff" and "soft" vibrational modes, within an adiabatic hypothesis assuming that the former modes are much faster than soft ones. In this framework, the spectrum can be rigorously expressed as a conformational average of different vibronic spectra, which are computed along the MD trajectory, from reduced-dimensionality quadratic Hamiltonians, built in the space of the stiff coordinates only, exploiting a generalization of the Vertical Hessian harmonic model (gVH) and a iterative application of projectors to remove all soft modes.² The latter are still accounted for, but only at classical level, through the conformational distribution sampled with classical MD runs, whose reliability is increased through the adoption of accurate Quantum-Mechanically Derived Force-Fields.³ Since it combines, through an adiabatic (Ad) approximation, a quantum gVH method with classical MD simulations the whole protocol has been named³ Ad-MD|gVH. As a first application, the Ad-MD|gVH method is tested on three different systems, each consisting in a solute, containing one or more π -conjugated chromophores, and a simple solvent. Both the dye's flexibility and the strength of its interaction with the solvent are increased along the series: N-methyl-6-oxyquinolinium betaine in water, an almost rigid solute, establishes moderate strength H-bonds with an aqueous solvent; di-thiophene in ethanol, which does not establish strong H-bonds. but presents a soft (torsional) mode effecting the π conjugation, and cyanidine, which is characterized by a similar flexibility but it additionally bears five rotatable oxydrilic groups, able to establish a more complex H-bond network in water. The very accurate simulation of the experimental shapes without any phenomenological broadening will be presented and all the results discussed also with respect to some details of the proposed method.

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Computational Modelling of Exciton Localization in Self-Assembled Perylenes

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Self assembled Organic conjugated materials (e.g. Perylenes) have recently received scientific interest due to the tunability of their photophysical properties that elected them as possible candidates for several technological application, ranging from the display technologies to photovoltaics devices. As established for the first time by Kasha, the photophysical properties of supramolecular aggregates are shown to be mainly related to the packing geometries of the molecular aggregates. Indeed, the maximum absorption results blue shifted when the geometrical arrangement is "side-by-side" (H aggregates). On the other hand, a red shift is predicted when the aggregation geometry is "head-to-tail" (J aggregates).

The PDI molecule (Figure 1) spontaneously adsorb on several semiconductors forming π -stacked H aggregates. This behavior is demonstrated by the intensity reversal between the 0-0 and the 0-1 vibronic bands in the optical absorption of the PDI sensitized film compared to the one registered in low concentration solution. However, to have an efficient electron/hole injection by these photoexcited aggregates into the semiconductor, the nature (localized Frenkel-type or charge transfer (CT)-like) and delocalization (i.e. exciton length) of the exciton, as well as its sub-picosecond photo-physics play a central role. The effects of aggregation on excited states properties of the self assembled PDI H aggregates were studied in a multilevel approach that combines first principle Density Functional Theory (DFT), Time-dependent DFT (TDDFT), one particle transition density matrix analysis and classical Molecular Dynamic (MD) simulation. Our multiscale protocol aims at modelling the excited state properties of PDI aggregates and describing the exciton character and delocalization as a function of the thermal motion and the aggregates size. With our approach we demonstrate that even if the dynamic effects do not remarkably affect the calculated position and shape of the absorption spectrum, the thermal motion favors the appearance of several low-energy states of charge transfer character (dark states) that are potentially involved in the ultrafast exciton relaxation dynamics.

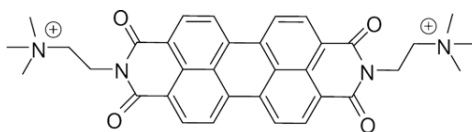


Figure 1. Chemical Formula of the PDI monomer dication

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Performance of DFT Functionals for Calculating Second-Order Nonlinear Optical Properties of Merocyanine Dyes

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Novel merocyanine dyes^{1,2} (Figure 1) exhibiting giant first hyperpolarizabilities have been synthesized and characterized by means of Hyper-Rayleigh Scattering (HRS) measurements and DFT calculations. These latter provide a fundamental understanding of the various factors governing the magnitude of the 2nd order NLO responses of the dyes, including donor/acceptor contributions, size of the conjugated linker and frequency-dispersion effects. The performances of various exchange-correlation functionals (XCF), including long-range corrected XCF, are discussed regarding their ability to reproduce the experimental data. The effect of the amount of exact HF exchange, the reliability of the two-state approximation and the range separation parameter optimization are also investigated.

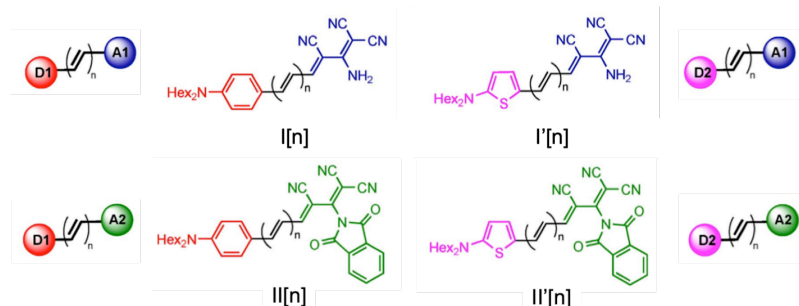


Figure 1. Structures of the tricyanopropylidene-based merocyanines studied herein. The length of the polyenic chain varies from $n = 0$ to $n = 4$.

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How does the Baird rule fade?

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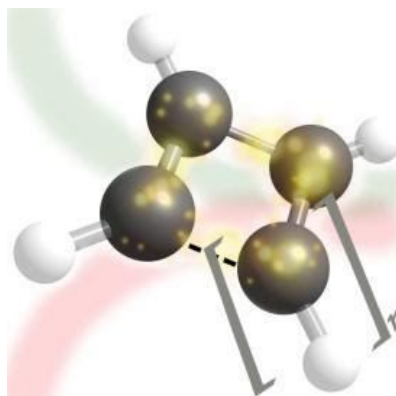
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Aromaticity is a multi-fold property and ill-defined concept that does not correspond to any physical observable. Diverse simple models have been designed together with aromaticity rules to study the aromatic character of molecules. The first and the most widely spread rule is the Hückel rule that anticipates a planar singlet $4N+2$ ($4N$) π -electron system to be aromatic (antiaromatic).¹ The Baird rule, complementary to Hückel's, predicts $4N$ ($4N+2$) π -electron system in its lowest triplet state to be aromatic (antiaromatic).² Baird claims the aromaticity decreases at the same speed with ring size. It has already been seen that the statement above is true if one applies Hückel rule for the singlet ground state.²



In this work, we have studied how the aromaticity rules fade away with the ring size in the C_nH_n annulene series ($n=4-18$, even number) taking into account the prediction using the Hückel Molecular Orbital (HMO) theory.³ We have analyzed several aromaticity indices among them FLU,⁴ BLA, BOA, I_{ring} ⁴ and AV_{min} ⁵ will be the most discussed. We have also discussed the effect of the computational method in the description of these annulene series using different density functional approximations with various percentage of exact exchange.

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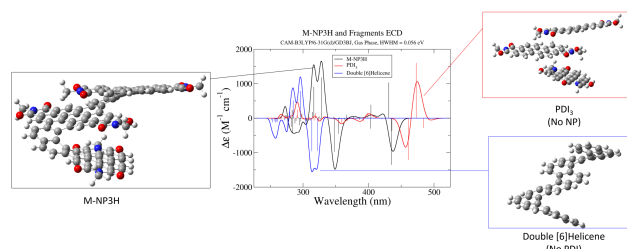
Exciton coupling on the ECD of perylene diimide helicenes rationalized with molecular fragments.

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The Naphthalene Perylene Diimide Helicenes family of compounds recently synthesized (NPXH, X=number of perylenes), exhibit very interesting properties with great applicability on the field of molecular electronics due to their extended π -delocalization and stability.^{1,2} In particular, a huge 15-fold enhancement of chiroptical response is observed for the trimer NP3H respect to the dimer NPDH at the region of 400 nm.² In order to understand this phenomenon, we performed electronic-structure and vibronic calculations that nicely reproduced the absorption and ECD spectra. Analysis of the electronic densities and natural transition orbitals show that the strong ECD signal of NP3H arise from four different states which mainly involve the helicene moiety, even though they usually absorb in the UV region.³ This amplification of the ECD signal is due to the exciton coupling between the helicenes, which is not possible in the dimer because there is only one of them. To support this thesis, we calculated the ECD spectrum for a number of simplified molecular fragments obtained by removing most of the PDIs atoms within NP3H structure (F1, F2 and Double[6]Helicene) or by removing the naphthalene cores (PDI₃). All the fragments nicely reproduce the strong bisignated couplet of NP3H whereas PDI₃ matches with the low-energy region (Figure 1). In summary, as far as the ECD response is concerned, the system can be described as a helix of helicenes. On the contrary, the PDIs play only a secondary role, affecting and stabilizing the molecular structure and the transition energies and enhancing the exciton splittings through the π -conjugation.

Figure 1. ECD spectrum of M-NP3H and its molecular fragments.

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Towards Computing the Quantum Dynamics of Proton Coupled Electron Transfer in Guanine-Cytosine Base Pairs in Chloroform

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In the past decade and a half, proton coupled electron transfer (PCET) has been posited as an important mechanism for excited state deactivation of DNA base pairs, thanks to the seminal *ab initio* studies by Domcke *et. al.* on a guanine-cytosine (GC) pair in the gas phase.¹ Recent time-resolved experimental work on GC pairs in chloroform has also indicated that this mechanism occurs in solution,² whilst TD-DFT calculations of GC in chloroform have indicated a minimum occurs on the charge transfer state and a small barrier occurs along the proton transfer coordinate, which do not appear in the gas phase.³ GC in chloroform is the simplest model system for understanding PCET in DNA, since the single pair decouples the effect of stacking and influence of the backbone, whilst chloroform possesses a similar dielectric constant to that in a DNA double helix. In this work we report our initial progress in developing a model Hamiltonian from TD-DFT calculations for use with quantum dynamics simulations by ML-MCTDH to describe this PCET process for GC in chloroform. The approach is twofold: firstly, we must describe the transfer from bright excited states to the charge transfer minimum, and secondly, the transfer from charge transfer minimum to proton transfer minimum. The dynamics calculations will help to elucidate the interplay between excited states, and timescales for the transfer between them, as the process has been hypothesised to occur faster than experimental resolution.

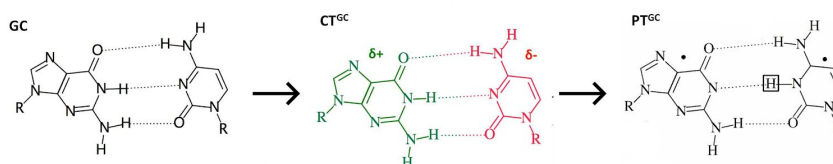


Figure 1. Proton coupled electron transfer for a GC base pair.

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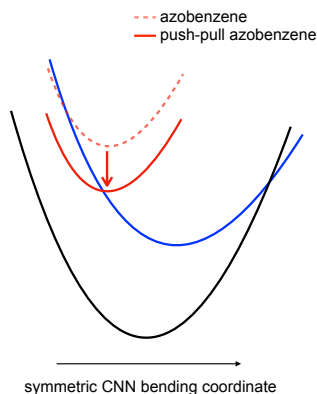
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Increased photoisomerization efficiency of push-pull azobenzenes resolved with semiclassical dynamics

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Azobenzene and its derivatives are known for their ability to undergo ultrafast *trans-cis* isomerization when irradiated with light. However, the high absorption energy of the bright $\pi\pi^*$ state, peaked at the UV, is a limiting factor for many applications (e.g., biological systems). Moreover, the photoisomerization quantum yield from S_2 ($\pi\pi^*$) is reduced with respect of that from S_1 ($n\pi^*$). Indeed, starting from the dark $n\pi^*$ state, the reactive coordinate mainly follows the torsion around the central N=N bond (productive mechanism), while excitation to the bright $\pi\pi^*$ state favors the symmetric CNN bending motion, leading to a cascade of S_2 - S_1 - S_0 non-reactive decays that do not involve torsion.¹ We have investigated the effects of some push-pull substituents on the azobenzene system, targeted both to red-shift the absorption energy and to improve the photoisomerization efficiency from the bright $\pi\pi^*$ state. Semiclassical dynamics simulations (cam-B3Lyp/6-31G*) were started from the second excited state ($\pi\pi^*$) of both *cis*- and *trans*- isomers of the pure azobenzene dye, as well as of two push-pull-substituted systems. The results have revealed that the main effect of this type of substitution is a significant red-shift of the $\pi\pi^*$ state, while the $n\pi^*$ state is almost unaffected. As a consequence, the S_2/S_1 crossing seam gets lower in energy (Figure 1). Therefore, after the decay to S_1 , the kinetic energy along symmetric bending is significantly reduced. The net effect of those phenomena is to favor the torsional motion after decay to S_1 , compared to the parent azobenzene molecule, increasing the quantum yield of the bright $\pi\pi^*$ state. The red-shift of the absorption of the bright state up to the visible range, together with the increased photoisomerization efficiency, opens the way for a wide range of application of push-pull azobenzene derivatives.



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Excited state classical dynamics based on accurate QM calculations: azobenzene $n\pi^*$ photoisomerization

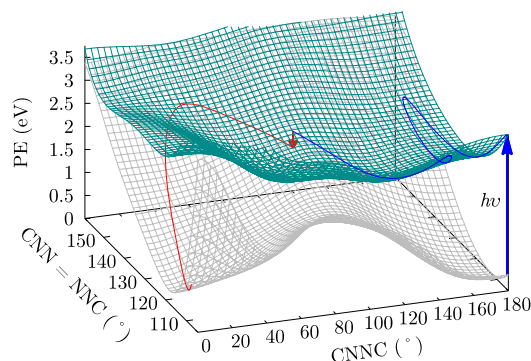
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Azobenzene and its derivatives are well known for their ability to behave as photoactuators, undergoing *trans-cis* photoisomerization. However, the simulation of non-adiabatic processes in relatively complex environments and nanosecond timescale is still not feasible with fully Quantum Dynamics methods. We describe here an efficient method for performing classical MD simulations of these photoprocesses based on accurate QM calculations, and its application to the challenging case of azobenzene $n\pi^*$ photoisomerization.

We selected the relevant degrees of freedom driving the photoisomerization process (*i.e.* the CNNC dihedral and the two CNN bending), and used accurate QM calculations (MS-RASPT2) to map the electronic potential energy (PE) and the non-adiabatic coupling (NAC) between the ground state (S_0) and the first excited state (S_1). Starting from AMBER General Force Field (GAFF)¹, we parametrized a new Class II FF for S_0 and S_1 . To this end, we fitted the QM PE hyper-surfaces (PESs) with 3D analytic functions, which were implemented, together with their gradients, in the atomistic Molecular Dynamics simulation software NAMD². This allowed to reproduce with the same accuracy more than one PES minimum, as well as to correctly describe the PES topology far from equilibrium geometries.

The method was assessed by means of geometry minimisations and semiclassical dynamics in the reduced 3D phase space of CNNC torsion and CNN bending angles, using the Tully algorithm³ for the non-adiabatic decay to S_0 . Results were compared with literature data⁴, which attested an excellent agreement. We are currently performing dynamics in the full phase space with improved PESs and a wider map of NACs vectors.



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/ Internal conversion in Cytosine Derivation in Gas Phase and Polar Solvent. A Quantum Dynamics study base on TD-DFT and LVC Hamiltonian.

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The UV photon absorption by DNA can induce photodamage of the genetic code. Fast non-radiative decays protect from these harmful processes.¹ In recent experimental articles^{2,3}, solvent and excitation wavelength effects on the ultrafast ! ! */ decay of two tautomers (oxo-amino and oxo-imino) of cytidine and 5-methyl cytidine were studied. The results show different decay times for different tautomers and two possible decay paths for different excitation wavelengths that were tentatively ascribed to the population of different type of n! *. From the computational point of view, a full quantum dynamical (QD) study of the decay process of cytosine at atomic level is still lacking,⁴ although QD effects are expected to be more and more important as the time-resolution of state-of-the-art experiments reaches the <30 fs timescale.⁵

In this study, 1-methyl-cytosine and 1,5 di methyl-cytosine were used as a model for cytidine and 5-methyl-cytidine respectively. For each molecule and solvent, we parametrized a specific Linear Vibronic Coupling (LVC) model from TD-DFT calculations with an in-house code,¹ employing two different density functionals, namely CAM-B3LYP and PBE0, in combination with the 6-31+G(d,p) basis set. The polar solvent is described by polarizable continuum model (PCM). QD calculations were carried out with ML-MCTDH method as implemented in Quantics package considering all the vibrational modes. CAM-B3LYP predicts that excitation to leads to only a small population transfer to in gas that becomes vanishingly small in chloroform. At variance, PBE0 in both gas phase and chloroform predicts remarkable transfer of population to both by exciting either or . PBE0 results in chloroform appear in better agreement with the experimental observation that, upon photoexcitation at 260nm (populating both and), about 50% of population decays to a dark state.

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Theoretical Investigations on the Photophysics of Charge-Transfer (CT) Co-Crystals with Equivalent Crystal Structures

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Understanding structure-property relationship is essential in order to design materials with desirable features.¹ Charge-transfer (CT) co-crystals, constituted by a mixing of donor (D) and acceptor(A) moieties, have demonstrated various promising optoelectronic properties.² However, it is a challenge to predict properties of such systems because their properties are not only related with the intra- , but also with the intermolecular properties, which depend significantly on the mutual arrangements.¹

In the current work, four D-A co-crystals were rationally designed, comprising two distyrylbenzene (DSB) type electron donors and two dicyanodistyrylbenzene (DCS) type electron acceptors, which share isometric molecular structure. Remarkably, the four co-crystals presented virtually identical crystal structure in the intra-stack direction and strong intermolecular interactions. Despite of the similar crystal structure, the co-crystals present quite different PL quantum yields (from 0.30 to 0.75) and PL lifetimes. This result is the highest value reported for CT complexes so far.

Herein, we discuss the photophysics features that determine the different behavior of the co-crystals through a detailed (time-dependent) density functional theory, (TD)DFT, analysis. We observed that the w-tuned wB97XD functional using the Tamm-Dancoff approximation (TDA) approach showed to be able to describe the deactivation process for (CT) co-crystals with a good agreement with the experimental results. A non-negligible oscillator strength of the emitting state despite the intermolecular DO/AC frontier MO localization is a key factor for the bright fluorescence.

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Dark photochemistry formation of CPDs photoproducts

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Photochemistry refers to a chemical reaction triggered by light absorption, which, promoting the system in its excited manifold, open a new plethora of chemical possibilities different from the ground state reactivity. As far as the system is promoted in its excited manifold, excited state reactivity as the one described in a photochemical process can occur independently on how the system has been initially excited. In the specific case of excited state reactivity without light absorption, the situation fall in the realm of the so-called dark photochemistry, which describes excited state reactivity that will be normally triggered by light absorption but in which the triggering exciting event does not involve light-matter interactions^{1,2}. Performing both DFT-based and ab initio CASPT2//CASSCF computations, in the present contribution we studied an experimentally proposed dark-photochemistry process leading to the sensitization of the pyrimidine nucleobases cytosine and thymine.³ The mechanism involves the formation of a dioxetane-based melanin (2DO) fragment, that undertaking a thermal activated peroxide bond breaking can chemisensitize the pyrimidine nucleobases through a triplet-triplet energy transfer mechanism. Interesting, the interaction between 2DO and the nucleobase favors the chemiexcitation process, as reflected by the lower energy barrier toward peroxide bond dissociation computed for the 2DO-cytosine and 2DO-thymine systems than for the isolated 2DO molecule.

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Influence of the environment in the photobiology of nucleic acids

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Sunlight has reached Earth's surface since the formation of the planet. Nucleic acids that compose genetic material, the primordial ingredient of life, have been shaped by this irradiation, evolving to survive under the constant presence of UV photons reaching living beings.¹ However, it is also known that light can induce DNA damage either by direct absorption of light or via oxidative/reductive reactions with the environment. Unveiling the photostability and photodamage mechanisms, as well as their intrinsic competition, is not only of interest to understand the natural selection of the current DNA chemical structure, but also crucial to comprehend the insurgence of DNA lesions, in turn related to important diseases such as cancer.²

The use of cutting-edge experimental set-ups such as ultrafast time-resolved UV and IR spectroscopies coupled with state-of-the-art computational methods have paved the way to the fine comprehension of the subtle mechanisms that preserve or hurt DNA.³ In the present talk, I will highlight the role of modern computational techniques to understand the mentioned events. In particular, I will emphasize the use quantum-chemistry methods coupled with molecular mechanics (QM/MM) schemes to treat excited states in complex environments, deemed of utmost importance to describe DNA damage, photostability and photosensitization mechanisms.⁴⁻⁶

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Modeling tautomeric equilibria of cyanin and the resulting impact on its optical properties

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The equilibrium between protomeric tautomers in solution depends strongly on specific interactions with the solvent, including both electrostatic effects due to the dielectric environment, and the hydrogen bonding network in protic solvents such as water. In this work we compute the equilibrium between tautomers of cyanin-3-glucoside (C3G) in water. C3G is a common natural dye found in many flowers, fruits and vegetables, and is also a pH indicator, varying in colour due to gradual deprotonation with increasing pH. The order in which various sites lose a proton is not completely agreed upon in the literature, and it is likely that at neutral to high pH, several tautomers may coexist in solution. Furthermore, C3G presents a case in which the electronic structures of the tautomers can differ greatly so as to influence the optical properties and the colour of the dye.¹ The scheme implemented involves an 'alchemical' thermodynamic integration using density functional theory molecular dynamics. The integral of the energy with respect to the thermodynamic parameter is computed from its analytical form on-the-fly, removing the need for obtaining numerical derivatives from pairs of parallel simulations, as is routinely the case in previous works. This method could be further applied to other relevant systems such as nucleic acid bases, in which this type of proton transfer reaction has been linked to the appearance of DNA and RNA mutations.

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Flavylium dyes as near-infrared fluorophores

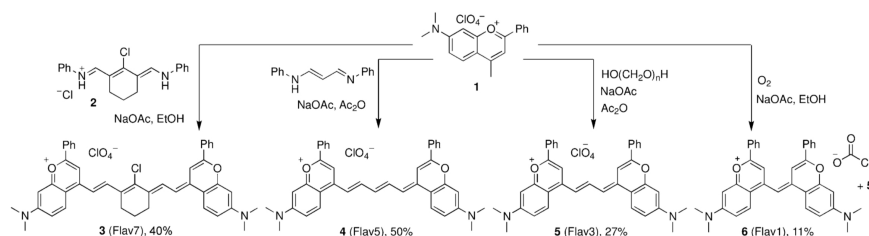
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Bright fluorophores in the near-infrared and short-wave infrared (SWIR) regions of the electromagnetic spectrum are essential for optical imaging *in vivo*. In this work, we present a theoretical investigation on a series of compounds that contain two dimethyl flavylium (Flav) heterocycles connected by 1,3, 5 or 7 methine units (=CH- groups) (see Figure 1).



Scheme 1. Synthesis of dimethylamino flavylium polymethine dyes 3–6.

Figure 1. Molecules investigated in this project.

The emission of these dyes is notably red-shifted compared to prevalent cyanine dyes, and expand the opportunities for imaging and detection at NIR and SWIR wavelengths.

I will demonstrate how decomposition of the computed excitations in terms of diabatic states can be extremely valuable in order to identify and quantify the nature of electronic transitions in the presence of several electron donor and acceptor fragments. Such decomposition is crucial to understand how extending the polymethine conjugation or changing the electron donor groups impacts the emission wavelengths of these dyes.

Characterization of the Lowest Excited States in PDI Aggregates

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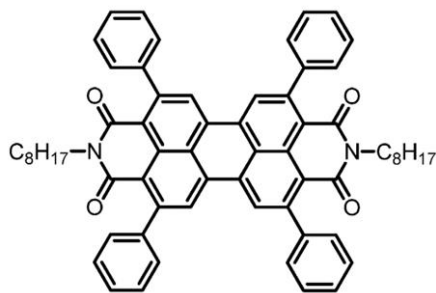
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Perylene-3,4:9,10-bis(dicarboximide) (PDI) and its derivatives are well known visible organic chromophores with excellent optoelectronic properties for energy and charge transport [1]. Moreover, their molecular rigidity results in robust thermal and photochemical stabilities, and strong absorption capabilities of visible and near-infrared (NIR) light. Photophysical properties of PDI aggregates are of special interest as light-harvesting materials in organic photovoltaics [2].

While low-lying singlet excitations of PDI have been largely investigated, much less is known about the triplet state. Despite that the triplet manifold is not initially accessible through photoexcitation, recent studies have identified spin triplets as the final photoproduct states upon exciton decay processes in PDI covalent dimers [3] and in the crystal [4].



1. Figure. PDI molecule studied in this work.

In the present work we aim to unravel the properties of the lowest excited states in molecular aggregates of PDI, with special interest on the lowest triplet state (T_1). To that end, we have computed vertical and adiabatic energy gaps and we have characterized the electronic nature of T_1 by means of exciton and spin delocalization, charge transfer contributions, and electronic couplings with the use of a variety of quantum chemistry methods and computational tools within the density functional theory (DFT) and its time-dependent version (TDDFT). Rationalization of the obtained results has been done with respect to the electronic structure properties of molecular states and the properties of low-lying excited singlets in molecular aggregates.

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Does the Baird Rule hold on Expanded Porphyrins?

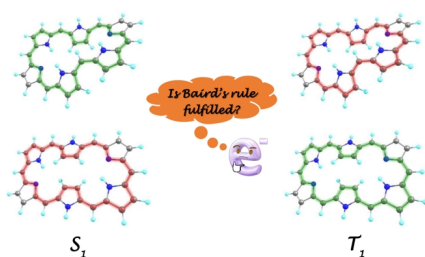
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In the last decade, expanded porphyrins have shown a conformational flexibility that allows them to achieve original motifs with specific aromatic, magnetic, and electric properties, emerging as a new promising class of molecules for the creation of topological switches.^[1-3] The aromaticity of expanded porphyrins is often determined from the topology, the spin state and the number of pi-electrons, following either Hückel's (singlet π -conjugated systems with zero or an even number of half-twists), Heilbronner's (singlet π -conjugated systems with an odd number of half-twists) or Baird's (triplets) rules. Recent works have reported experimental evidence that expanded porphyrins show a reversal aromaticity on the excited states as compared to their corresponding ground states.^[3] In this work, we report a theoretical investigation of the conformational switch between Hückel planar, singly twisted Möbius, and figure-eight conformations of [26]- and [28]-hexaphyrins. In all cases, the ground state and the lowest excited triplet state are studied. Using the electronic indices AV_{1245} ,^[6] and AV_{min} ,^[7] we show that the reversal of aromaticity induced by the change of the electronic state affects more the kinetics of these topological switches than the thermochemistry. We also show that the Baird rule is only qualitatively satisfied in these compounds, and there is a clear exception that does not satisfy it. We believe our results put forward the limited character of Baird's rule for large conjugated circuits.^[8]

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Poster presentations

Sp-hybridized all-carbon molecular structures: A challenge for density-functional approximations

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The recent synthesis of a C₁₈ monocyclic ring¹ constitutes a major breakthrough as a new all-carbon disclosed form, in addition to classical (carbon, diamond) and modern (fullerenes, graphene) allotropes. Many emerging applications in Chemistry and Materials Science, stimulated by this fascinating achievement, are thus expected in next years. These envisioned applications may be fostered and/or assisted by complementary theoretical studies. However, modern density functional theory approaches do not lead to the correct experimental polyynic structure and favor the cumulenenic one instead. We demonstrate here that this serious drawback can be solved² by recently developed range-separated (universal and nonempirical) schemes³⁻⁴, independently of which kind of functional is being applied (i.e., semilocal, hybrid, or double-hybrid).



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Counterion-Mediated Crossing of the Cyanine Limit in Crystals and Fluid Solution - Bond Length Alternation and Spectral Broadening Unveiled by Quantum Chemistry

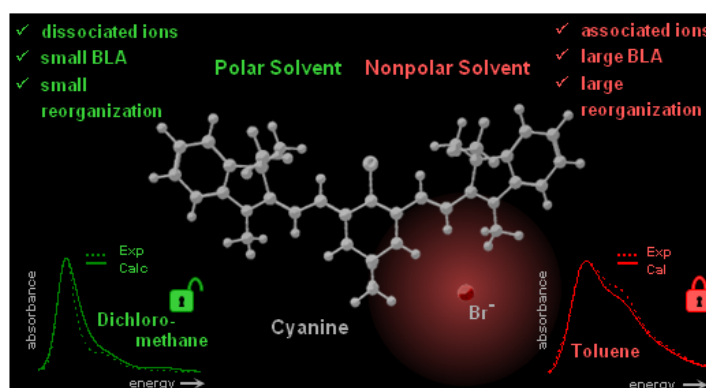
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Absorption spectra of Cyanine⁺Br⁻ salts show a remarkable solvent dependence in non-/polar solvents, exhibiting a narrow, sharp band shapes in dichloromethane but broad features in toluene; this change was attributed to ion pair association, stabilizing an asymmetric dipolar structure, similar to the situation in the crystal (P.-A. Bouit et al, J. Am. Chem. Soc. 2010, 132, 4328). Our density functional theory (DFT) based quantum mechanics/molecular mechanics (QM/MM) calculations of the crystals evidence the crucial role of specific asymmetric anion positioning on the lowering of the symmetry. Molecular dynamics (MD) simulations prove the ion pair association in non-polar solvents. Time-dependent DFT vibronic calculations in toluene show that ion pairing indeed stabilizes an asymmetric dipolar structure in the electronic ground state. This largely broadens the absorption spectrum in very reasonable agreement with experiment, while the principal pattern of vibrational modes is retained. The current findings allow to establish a unified picture on symmetry breaking of polymethine dyes in fluid solution.¹



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Photophysics of Innovative Organic Charge-Transfer Systems

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Charge Transfer (CT) states are of crucial importance in the functionality of organic materials for optoelectronics and energy conversion, being key element as donor-acceptor (DA) complexes, dyads, copolymers, co-crystals or interfaces. Although the principle parameters to tune the electronic CT properties are set,¹ the understanding of excited state ordering of CT and locally excited (LE) singlet and triplet states, intermolecular couplings, and their deactivation through internal conversion, inter-system crossing, fluorescence and phosphorescence are grand challenges of current research. Our activities focus on different aspects of excited state formation and deactivation in innovative intra- and intermolecular DA CT systems, which are here shortly reviewed, including dynamic CT formation at conical intersections,² DA polyads and nano-interfaces for photocatalysis,^{3,4} and highly-luminescent and stimuli-responsive mixed-stacked DA co-crystals.⁵

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Crossed 2D vs. Slipped 1D π -Stacking in Polymorphs of Crystalline Organic Thin Films: Impact on the Electronic and Optical Response

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The device functionality of small molecule-based organic optoelectronics depends strongly on the intermolecular arrangements and on morphological factors. This becomes apparent if the optical or electric response of different polymorphs of the same materials are compared. In particular, 2D arrangements – gathered via edge-to-face (herringbone) or slipped face-to-face (brickwork) packing motifs - were early realized as advantageous for efficient charge transport.

Here, we report on the successful x-ray diffraction structure analysis of two polymorphic phases (B = blue, G = green) of a dicyano-distyrylbenzene derivative, being a crucial step for the understanding of the electronic and optical response of the final devices. B- and G-phase show dramatically different molecular 2D crossed ! -stack vs. 1D slipped ! -stack packing motifs, which result in drastically different device functionalities, i.e. the (anisotropic) electronic and optical response. All differences are fully elucidated by means of (TD)DFT, embedded in a QM/MM scheme, being all together a crucial step towards future device analysis of novel third generation organic optoelectronic materials.

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Novel U-Shaped D-A-D π -conjugated Systems with Mechanochromic Properties: An Experimental and Theoretical Vibrational Spectroscopic Investigation

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π -conjugated compounds have been widely studied in the last few decades due to their huge field of application in organic electronics. Specifically, stimuli-responsive π -conjugated materials which are sensitive to external stimulus (i.e., temperature, pressure, etc) have several uses like sensors, probes and security inks, for example.¹ In this work, we study two U-shape Donor-Acceptor-Donor (D-A-D) systems that are found to exhibit interesting thermal- and pressure-dependent properties.² They consist on two different conformers of phenothiazine-dibenzo[*a,j*]phenazine-phenothiazine which differs from the position of the phenothiazine respect to the dibenzophenazine central core. Compound 1R is the equatorial-equatorial conformer and 1Y is the axial-axial conformer (Figure 1). The dibenzophenazine group acts as an electron-acceptor whereas the phenothiazine unit acts as an electron-donor. It has been reported that this U-shape D-A-D compound shows a multi-active color changing in 3 steps and their luminescence changes with temperature, pressure and acid exposition.² In this work, we aim to elucidate how the external stimuli (i.e. temperature, pressure, acid ambient) affects the molecular structure at both intra- and intermolecular level. To this end, we use UV-Vis absorption, Raman (Figure 1) and Infrared spectroscopy experiments in combination with DFT calculations.

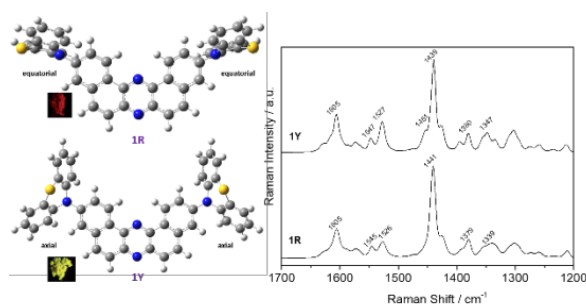


Figure 1. Chemical structure of 1R and 1Y compounds and their corresponding experimental Raman spectra.

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Photophysics of Dual Emissive Organic Donor- π -Acceptor Molecules

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Dual emissive organic materials have gained immense research interest due to their applications in energy conversion, sensing and imaging. An understanding of the photophysical processes that triggers the dual emission in organic molecules is crucial to accelerate their widespread applications. Studies revealed that the different possible routes for the dual emission are S_2 emission, T_1 emission, twisted intramolecular charge transfer (TICT), excited state (ES) planarization, excited state intramolecular proton transfer (ESIPT), ESPT, ES isomerization, etc. On the other hand, the dual emission depends greatly on polarity and viscosity of the solvent and donor/acceptor strengths.

The Donor (D) - acceptor (A) systems, with substituted amino group as donor and triazine group based moiety as an acceptor, were elegantly used as thermally activated delayed fluorescence (TADF) emitters in organic light emitting diodes. Very recently, triazine-based TADF molecules were optimized for the use as photocatalysts polymerization reaction. i.e. compounds **1** and **2** (in Figure 1) which different in the donor group.^{1,2} Here, we have explored the photophysics of **1** and **2** in different solvents, as well condensed environment, reporting on tunable fluorescence with dual emission.³ Time-dependent density functional theory (TD-DFT) calculations are used to reveal the underlying electronic properties, which give rise to dual emission in **1** and **2**. Both **1** and **2** display strong positive solvatochromism with increase in polarity of the solvents and exhibit intriguing dual emission in DMSO solution. Both time-resolved fluorescence measurement and TDDFT studies corroborated the dual emission of **1** and **2**. On the other side, in the condensed environment we observed tunable emission upon formation of nanoparticles.

Our combined spectroscopic and TD-DFT studies are seen as a crucial step to understand the basic photophysics of these TADF materials, to further advance their use in opto-electronic applications.

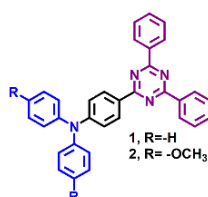


Figure 1. Chemical structures of **1** and **2**.

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X-rays spectra of nanodiamonds

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Nanodiamonds are found in meteorites and they are also synthesized in laboratories. Formation of diamonds at planetary interior conditions was confirmed in Neptune, Uranus and exoplanets. Nanodiamonds were detected around some stars using infrared telescopes. They also exist in the interstellar medium. Using density functional theory methods we calculate the K-edge X-ray absorption spectra of two larger tetrahedral nanodiamonds: C₂₆H₃₂ and C₅₁H₅₂. We also study and test our methods on methane, a smallest C-H tetrahedral structure for which X-rays laboratory data are available. We consider detection of nanodiamonds by the Arcus, a proposed X-ray telescope.

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Van der Waals interactions in Nonlinear Optical Switches

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Molecular systems which exhibit within their isomers large differences on their nonlinear optical properties (NLOPs) are called nonlinear optical switches. These systems have several applications in optoelectronics, which include for example data storage, information processing and optical communications. In particular, among these molecules are the azobenzene derivatives, which, upon irradiation of light, are able to switch between the more stable *trans*-isomers (E) to the less stable *cis*-isomers (Z) exhibiting a large contrast in their NLOPs. Starting from an azobenzene scaffold, using appropriate substituents, it is possible to design several classes of molecular switches. In order to develop novel families of functional molecules it is necessary to deeply understand how their optical response is connected with their chemical structure.

In the work of Schweighauser et al. [1], it has been observed experimentally and computed by means of Density Functional Theory (DFT) that, in azobenzene-based molecules with large substituents, intramolecular Van der Waals (VdW) interactions stabilize thermodynamically the Z isomers. In our study, we extended the characterization of these molecules computing their ground state at DFT level. Several Density Functional Approximations (DFA) have been tested, combining different corrections able to reproduce VdW interactions. Moreover, we computed the NLOPs of these systems, showing how a treatment of VdW interactions at different level of approximation influences the contrast on the hyperpolarizability between the E and Z isomers. This analysis allow the identification the DFAs able to accurately reproduce the nonlinear optical response of azo-molecules with large organic substituents. Furthermore, it gives theoretical insights for developing a new kind of molecular switches.

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Predicting fluorescence quantum yields for molecules in solution: A critical assessment of the harmonic approximation and the choice of the lineshape function

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For the rational design of new fluorophores, the reliable prediction of fluorescence quantum yields from first principles is necessary. However, efficient computational approaches for predicting transition rates usually assume that the vibrational structure is harmonic. While the harmonic approximation has been used successfully to predict vibrationally resolved spectra and radiative rates, its reliability for non-radiative rates is more demanding. Since non-adiabatic transitions convert large amounts of electronic energy into the vibrational energy, the highly excited final vibrational states deviate greatly from harmonic oscillator eigenfunctions. We employ a time-dependent formalism to compute radiative and non-radiative rates for transitions and study the dependence on model parameters. For several coumarin dyes we compare different adiabatic and vertical harmonic models (AS, ASF, AH, VG, VGF, VH), in order to dissect the importance of displacements, frequency changes and Duschinsky rotations and we analyzed the effect of different broadening functions (Gaussian, Lorentzian or Voigt). Moreover, to assess the qualitative influence of anharmonicity on the internal conversion rate, we develop a simplified anharmonic model. We comment on the reliability of these models in view of the potential errors introduced by the harmonic approximation and the phenomenological width of the broadening function.

Carbazole-based Diradicals for Dynamic Covalent Chemistry

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Dynamic covalent chemistry (DCC) is focused on the creation of structural scaffolds based on chemical components that interact through strong but reversible bonds. In fact, dynamic covalent bonds receive lot of attention because of their unique feature to become reversible under mild conditions.¹ ! ! conjugated diradical compounds has emerged as essential building blocks in DCC.² In this work, we will review our most recent works on the formation of stimuli-responsive cyclophanes by self-assembly of carbazole-based diradicals. To this end, we use a combined experimental and theoretical approach that links vibrational spectroscopy with DFT calculations. In this sense, it is interesting to note that we have recently demonstrated the potential of a para-substituted carbazole with terminal dicyanomethylene (DCM) groups to act as building blocks in DCC.³ This quinoid carbazole monomer transforms to a macrocycle cyclophane upon soft external stimuli (temperature, pressure, light), showing strong chromic features. In addition, we have also recently explored how the different DCM substitution position affects the interesting chromoactive properties of carbazole compounds.⁴ Finally, we are currently exploring the effect of the elongation of the carbazole backbone on the formation of stimuli-responsive cyclophanes.

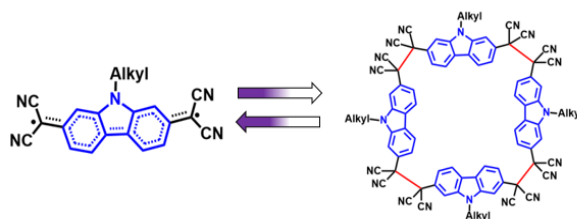


Figure 1. Equilibrium between an isolated carbazole-based monomer ascribed to the open-shell (OS) singlet state and its corresponding cyclophane aggregate.

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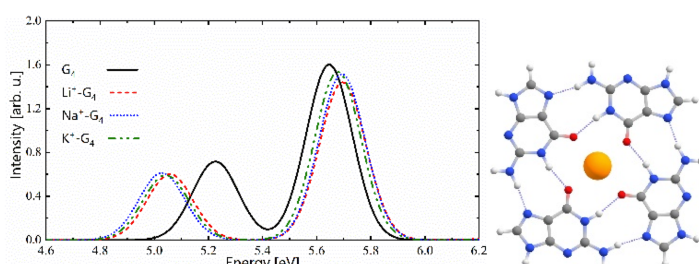
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Alkali metal cations impact on the excited states properties of the guanine quartet

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$LE + CT = LE + CT_{neighbor} + CT_{diagonal} + CT_{metal} = 1$ At the end of the eukaryotes chromosome, guanine (G) rich telomeric region plays an important role in facilitating the protection of the genetic material by organizing guanines into biologically relevant nanostructures called G-quadruplexes [1]. These structures can accommodate various metal ions into their central cavity to improve stability. They are consisted of multiple stacked G-quartets (G_4) constructed with four guanine molecules each, connected by framework of eight Hoogsteen type hydrogen bonds (Fig. 1a). Guanine show self-organization tendency towards G_4 structures in the absence of the DNA backbone. This impose G_4 structures to be used as scaffolds to control self-organization of the materials [2]. In this contribution we study excited states of G_4 and its complexes with alkali metal ions ($M-G_4$, $M=Li^+$, Na^+ , K^+) by employing time-dependent density functional theory [CAM-B3LYP/6-31G(d) at M06-2X/6-31+G(d,p) optimized geometries]. We show that within this multichromophoric system, electronic transitions have both local excitation (LE) and charge transfer character (CT). Although many excited states have high CT content there is no net charge separation observed upon excitations. Monomer-like combinations of L_a and L_b transitions are observed for the S_1 - S_4 and S_5 - S_8 states respectively. L_a and L_b transitions are red- and blue-shifted upon introducing alkali metal cations (Fig. 1b). Moreover, L_a and L_b transitions are not sensitive to the cation ionic radius. CT content of the excited states (diagonal and neighboring contributions) is also modulated similarly with all cations studied here. At the geometries of the S_1 minimum in all of the examined complexes, we find localized excitation on one of the guanine monomer units. This implies that an excited state lifetime of G_4 should be similar to the one of an isolated guanine molecule. Distortions of the complex geometries at the S_1 minimum are causing that complexes have different vertical excitations energies, while their adiabatic energies have very similar values. Therefore, cations are able to modify fluorescence spectra maxima positions of these complexes.

Figure 1. a) $M-G_4$ structure; b) Electronic absorption spectrum of the $M-G_4$ complexes.

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Nonlinear optical properties of spirocyclohexadine photochromes

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1,3-indandione-derived spirocyclohexadine compounds are a new class of photochromes showing sensitivity to both UV and visible lights. We investigate here their second-order nonlinear optical properties (NLO) by means of density functional theory. We show that these compounds should display a large first hyperpolarizability variation upon commutation between their cyclic spiropyran (SP) and their merocyanine (MC) forms. We also demonstrate that significant enhancement of the NLO response of the open merocyanine form, as well as of the NLO contrast, can be achieved by means of appropriate chemical substitution, making these derivatives highly appealing for potential integration in photo-responsive NLO devices.

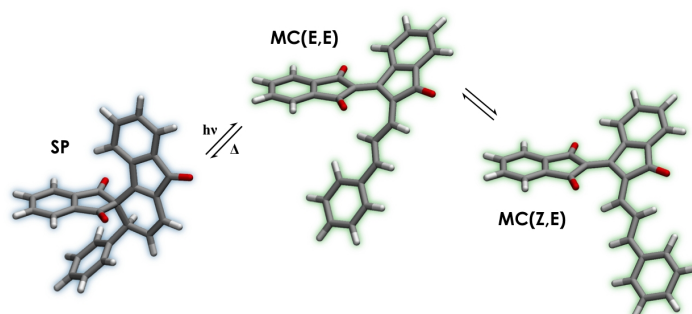


Figure 1. Photochromic reaction of 1,3-indandione-derived spirocyclohexadine compounds.

Tailoring π -conjugation and vibrational modes to steer onsurface synthesis of pentalene-bridged ladder polymers

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The rational design of increasingly complex electronic materials for molecular electronics and quantum technologies has been an active field of research in organic electronics. Particularly appealing are π -conjugated polymers¹ due to their relevant optical and electronic properties stemming from the delocalization of the π -electrons, which are the key for the incoming revolution of transparent and plastic electronics. However, despite great advances in the field from the synthetic point of view, we still lack 1D π -conjugated polymers that feature intrinsic ultra-narrow or even zero bandgaps, accomplishing the dream of engineering intrinsic metallic organic polymers².

Recent development of on-surface synthesis opened a novel strategy to synthesize a new class of intrinsically quasi-metallic one-dimensional (1D) π -conjugated polymers featuring topologically non-trivial quantum states^{3,4}. Furthermore, the fundamental relation between quantum topology, π -conjugation and metallicity of the polymers was revealed². Thus, it bridges the two distinct worlds of topological band theory (condensed matter physics) and π -conjugation polymer science (chemistry), which may stimulate new routes towards a design of organic polymers with unprecedented material properties (very low bandgap and magnetic properties).

In this work, we employ quantum-mechanical calculations for the description of structural and electronic properties of π -conjugated ethynylene bridged polymers^{3,4}. Additionally, we introduce novel synthetic strategy forming π -conjugated ladder polymers with nonbenzenoid pentalene bridges by exploiting the relation between π -conjugation, topological phase and vibrational modes of the polymer. Selected vibrational mode of ethynylene bridged bisanthene polymer is shown to be the key feature allowing the cyclization of ethynylene into pentalene linker, which is not observed in topologically trivial anthracene polymer. Finally, we present reaction mechanism highlights differentiating anthracene and bisanthene π -conjugated ethynylene bridged polymers, leading to successful cyclization in bisanthene but prevent the reaction on anthracene polymer completely, which is in direct agreement with experiments.

This work provides insight into experimentally observed properties in these novel systems and offers the possibility to qualitatively predict molecules suitable for on-surface tailored molecular chains.

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Structural Dynamics of Carbon Dots in Water and N, N-Dimethylformamide Probed by All-Atom Molecular Dynamics Simulations

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Carbon quantum dots (CDs) are considered 0D members of the family of carbon nanostructures. CDs are quasi-spherical particles with the size below 10 nm in all dimensions (typically 2–3 nm). Their structure may range from “amorphous” up to “crystalline” state with multilayer-graphene core. The core of CDs is surrounded by a shell containing various functional groups.² Due to low-cost preparation, biocompatibility, low toxicity and tunable fluorescence, CDs represent a perspective material for countless applications including bioimaging, biosensing, theranostics, etc.² Although CDs have been extensively experimentally studied, many questions still remain to be answered including the mechanism of fluorescence, internal dynamics, etc.³ In addition, the nature of interaction of CDs with various biostructures should be understood. Molecular dynamics (MD) simulations, enabling very fine atomistic and femtosecond resolutions simultaneously, could provide useful insights into the behavior of CDs. An efficient procedure for performing MD simulations of CDs is presented. More specifically, we developed a builder for generating crystalline CDs of a desired size and with various coverage of various oxygen-containing surface groups and we analyzed the behavior of various models of CDs differing in size, surface functional groups, and degrees of functionalization in water and dimethylformamide (DMF) by MD simulations. These simulations allowed us to analyze the internal dynamics of individual layers of CDs and to evaluate the role of surface functional groups on CDs stability. Currently, the presented tool enables simulations of CDs with oxygen and nitrogen containing surface groups in complex environments.

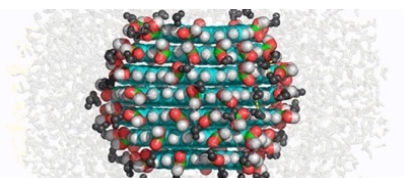


Figure 1. The representative model of oxygen functionalized quasi-spherical carbon quantum dot, studied by molecular dynamics simulations in water.

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Wave function overlap based assignment of UV absorption spectra and state specific analysis of solvation effects

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Overlaps between many-electron wave functions play an important role in photochemical studies as they offer an intuitive and straightforward way to track the electronic character of the states along different nuclear geometries without the need for complex diabaticization procedures.¹ One example of a problem where tracking the electronic character of many states is required is the theoretical assignment of electronic spectra of polyatomic molecules.

In this contribution, we propose a procedure based on the computation of electronic wave function overlaps for automatically determining the character of electronic transitions and apply it to the study of UV spectra of DNA bases in the gas phase and in the aqueous environment. Spectra are generated using the nuclear ensemble method in the gas phase and in solution and the electronic states at all nuclear geometries are assigned based on overlaps with a set of reference states defined at the ground state minimum geometry. This allows a state specific analysis of solvation effects. Solvent-solute electrostatic interactions are state specific and strongly destabilize nRyd states, and to lesser extent $\pi\pi^*$ and π Ryd states while $\pi\pi^*$ states are slightly stabilized.

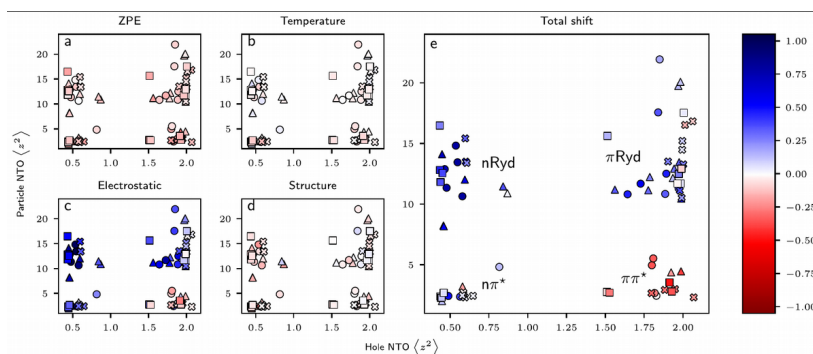


Figure 1. Effects of solvation on excitation energies for different types of electronic states of DNA nucleobases in the 190-350 nm range.

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Anti-Kasha nitrogen photoelimination from diazoalkanes

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Nitrogen elimination from diazoalkanes is a well-known reaction, which can easily be induced both thermally and photochemically.^{1,2} In this work we present a photochemical study of diazo compound **1**. Experimentally, it was observed to have a pronounced anti-Kasha photochemistry, as it gives greater yield of nitrogen elimination after UV excitation than after VIS excitation. Also, an anti-Kasha fluorescence was observed.

Nonadiabatic surface hopping dynamics was used to elucidate the photochemical behavior of **1**. To simulate VIS and UV excitations, the dynamics was initiated in corresponding energy windows, i.e. in the S_1 and S_2/S_3 states respectively. In both types of simulations, the S_1/S_0 CI was easily reached by elongation of the CN bond. We identified the anti-Kasha pathway of nitrogen elimination in around 30 % of trajectories initiated by UV excitation. The source of anti-Kasha fluorescence was also identified in around 4 % of UV-initiated trajectories and confirmed by excited-state optimization.

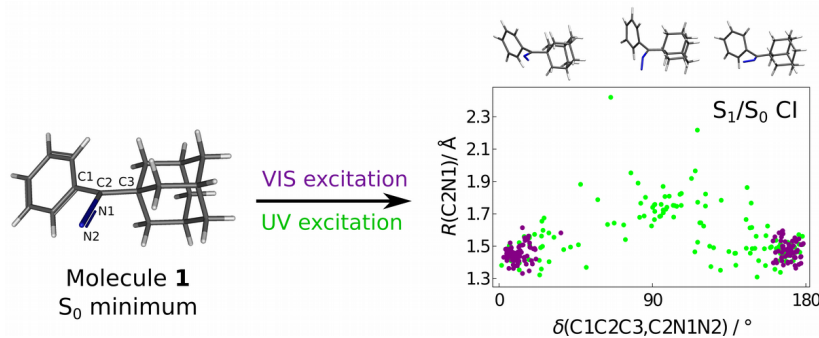


Figure 1. The distribution of CN bond length and two-plane angle in the vicinity of S_1/S_0 CI seam, obtained from the surface hopping dynamics of **1**. The dynamics was initiated by excitation of S_0 minimum ensemble to S_1 (VIS) and S_2/S_3 (UV) states.

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Mechanisms and kinetics of free radical reactions in non-buffered and buffered aqueous solutions

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We investigate computationally and experimentally the mechanisms and kinetics of reactions of α -hydroxyalkyl radicals and hydrogen atoms with haloorganic substrates, such as haloacetates (XAc^-) and 5-bromouracil (BrU).¹⁻³ The reactions are carried out in non-buffered and buffered (bicarbonate or phosphate) aqueous solutions. In these systems, the free radicals normally act as reducing agents bringing about the dehalogenation of the haloorganic substrates. Since the rate-determining step involves the deprotonation of the radical, addition of the buffers as the external proton acceptors is expected to increase the reaction rate and dehalogenation yields. Density functional theory calculations confirm that the transfer of the electron from the radical to the substrate takes place *concurrently with* the transfer of the proton from the radical to the buffer anion, water solvent or substrate. This is the hallmark of the *proton-coupled electron transfer* (PCET), a highly efficient mechanism of charge transfer indispensable for living matter and numerous man-made processes.⁴ The radical chain reaction which accompanies the PCET markedly increases the dehalogenation yields. The reaction pathways in competition with the PCET include hydrogen or halogen atom abstractions, and free radical substitutions and additions. In case of BrU, we attempt to explain a puzzling inhibition of the reaction that is observed in the presence of the phosphate buffer. The dominant reaction channels typically exhibit negative apparent activation energies, and so accurate modelling of the kinetics remains challenging. For this reason, we carried out an investigation of the performances of 18 density functionals for modelling the mechanisms and kinetics of the aqueous phase reactions between the α -hydroxyisopropyl radical and 9 organic substrates.¹ We found that M06-D3 and PBE0-D3 exhibit the best performance according to the lowest minimum absolute errors (1.10 and 1.26 kcal mol⁻¹ in the Gibbs free energies of activation), and M06-D3, M06-2X-D3 and MN15 according to the largest Pearson correlation coefficients (0.95, 0.94, and 0.94). Finally, we also consider the reactions of the hydrogen atom under similar conditions. The prospect of PCET from the hydrogen atom is especially fascinating as it entails the disintegration of the atom to the constituting proton and electron, which would thus represent the most fundamental instance of the PCET process.

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Program

from: to: 31.1.2020, Friday 1.2.2020, Saturday

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|-------|-------|------------------|---------------------|
| 08:00 | 08:20 | REGISTRATION and | |
| 08:20 | 08:40 | OPENING | |
| 08:40 | 09:00 | I1 | I3 |
| 09:00 | 09:20 | Tomica Hrenar | Nada Došlić |
| 09:20 | 09:40 | G1 | P1 |
| 09:40 | 10:00 | G2 | P2 |
| 10:00 | 10:20 | G3 | P3 |
| 10:20 | 10:40 | COFFEE BREAK | P4 |
| 10:40 | 11:00 | | COFFEE BREAK |
| 11:00 | 11:20 | M1 | |
| 11:20 | 11:40 | M2 | E1 |
| 11:40 | 12:00 | M3 | E2 |
| 12:00 | 12:20 | M4 | E3 |
| 12:20 | 12:40 | M5 | ROUND TABLE |
| 12:40 | 13:00 | M6 | |
| 13:00 | 13:20 | | CLOSING |
| 13:20 | 13:40 | LUNCH | |
| 13:40 | 14:00 | | lunch (city center) |
| 14:00 | 14:20 | T1 | |
| 14:20 | 14:40 | T2 | |
| 14:40 | 15:00 | T3 | |
| 15:00 | 15:20 | T4 | city tour |
| 15:20 | 15:40 | T5 | |
| 15:40 | 16:00 | POSTER SESSION | |
| 16:00 | 16:20 | and | |
| 16:20 | 16:40 | COFFEE BREAK | |
| 16:40 | 17:00 | I2 | |
| 17:00 | 17:20 | Silvije Vdović | |
| 17:20 | 17:40 | D1 | |
| 17:40 | 18:00 | D2 | |
| 18:00 | 18:20 | D3 | |
| 18:20 | 18:40 | D4 | |
| 18:40 | 19:00 | | |
| 19:00 | | symposium dinner | |

sessions:

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| Graphene-based and bio-materials | G |
| Computational methods and theory | T |
| Optimizing material properties and challenges in organic electronics | M |
| Dynamics in the excited state | D |
| Photophysics and photochemistry of organic and biological systems | P |
| Characterizing electronic (excited) states | E |

Invited talks:

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|---------|--------|----|---|
| Tomica | Hrenar | I1 | Molecular dynamics simulation of water on graphene |
| Silvije | Vdović | I2 | Excited State Dynamics of β -Carotene Revealed Utilizing Ultrafast Laser Spectroscopy |
| Nada | Došlić | I3 | Ultrafast electronic excitations in π -conjugated compounds |

Contributed talks:

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|-------------|-------------------|----|---|
| James | Green | D1 | Towards Computing the Quantum Dynamics of Proton Coupled Electron Transfer in Guanine-Cytosine Base Pairs in Chloroform |
| Flavia | Aleotti | D2 | Increased photoisomerization efficiency of push-pull azobenzenes resolved with semiclassical dynamics |
| Lorenzo | Soprani | D3 | Development of a method for performing MD simulations based on accurate QM calculations: azobenzene $n\pi^*$ photoisomerization |
| Martha | Yaghoubi Jouybari | D4 | $\pi\pi^*/n\pi^*$ Internal conversion in Cytosine Derivation in Gas Phase and Polar Solvent. A Quantum Dynamics study base on TD-DFT and LVC Hamiltonian. |
| Olatz | Uranga | E1 | Flavylium dyes as near-infrared fluorophores |
| Maria | Zubiria Ulacia | E2 | Characterization of the Lowest Excited States in PDI Aggregates |
| Eduard | Matito | E3 | Does the Baird Rule hold on Expanded Porphyrins? |
| Javier | Sanz Rodrigo | M1 | From triangle-shaped radicaloids to molecular emitters for TADF-based OLEDs |
| Giacomo | Londi | M2 | Multiple Charge Transfer States in Donor–Acceptor Heterojunctions with Large Frontier Orbital Energy Offsets |
| Alexandra | Harbuzaru | M3 | Fused Quinoidal Oligothiophenes Imides with High Electrical Conductivity |
| Yoann | Olivier | M4 | Resilience to conformational fluctuations rather than planar backbones drives conjugated polymer materials with low-energy disorder. insights from atomistic simulations. |
| Sergio | Gómez-Valenzuela | M5 | Theoretical study of Covalent Organic Frameworks based on C3-symmetric Central Cores |
| Gabriele | D'Avino | M6 | Chasing the “Killer” Phonon Mode for the Rational Design of Low-Disorder, High-Mobility Molecular Semiconductors |
| Silvio | Osella | G1 | Hybrid materials for artificial photosynthesis |
| Piotr | Blonski | G2 | Anchoring of single-platinum-adatoms on graphene derivatives |
| Sai Manoj | Gali | G3 | Graphene oxide and functionalized graphene oxide as humidity sensors |
| Juan Carlos | Roldao | P1 | Theoretical study on the Photophysics of Charge-Transfer (CT) Co-Crystals with Equivalent Crystal Structures |
| Angelo | Giussani | P2 | Dark photochemistry formation of CPDs photoproducts |
| Antonio | Frances Moneris | P3 | Influence of the environment in the photobiology of nucleic acids |

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|---------|-----------------|----|--|
| Sara | Laporte | P4 | Modeling the tautomeric equilibria of cyanin and the resulting impact on its optical properties |
| Giacomo | Prampolini | T1 | The Ad-MD gVH method: computing electronic spectra of flexible molecules interacting with an environment |
| Alekos | Segalina | T2 | Computational Modelling of Exciton Localization in Self-Assembled Perylenes |
| Laurie | Lescos | T3 | Performance of DFT functionals for calculating second-order nonlinear optical properties of merocyanine dyes |
| Irene | Casademont Reig | T4 | How does Baird rule fade? |
| Daniel | Aranda Ruiz | T5 | Exciton coupling on the ECD of perylene diimide helicenes rationalized using molecular fragments |

Posters:

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|---------------|---------------------------|----|---|
| Johannes | Gierschner | 1 | Counterion-Mediated Crossing of the Cyanine Limit in Crystals and Fluid Solution -Bond Length Alternation and Spectral Broadening Unveiled by Quantum Chemistry |
| Johannes | Gierschner | 2 | Photophysics of Innovative Organic Charge-Transfer Systems |
| Begoña | Milián Medina | 3 | Crossed 2D vs. Slipped 1D π -Stacking in Polymorphs of Crystalline Organic Thin Films: Impact on the Electronic and Optical Response |
| Sara | Fernández-Palacios Campos | 4 | Novel U-shaped D-A-D π -conjugated Systems with Mechanochromic Properties: An Experimental and Theoretical Vibrational Spectroscopic Investigation |
| Santosh Kumar | Behera | 5 | Photophysics of Dual Emissive Organic Donor- π -Acceptor Molecules |
| Goranka | Bilalbegovic | 6 | X-rays spectra of nanodiamonds: density functional theory |
| Carmelo | Naim | 7 | Study of Van der Waals interactions in Nonlinear Optical Switches |
| Margarita | Bužančić | 8 | Predicting fluorescence quantum yields for molecules in solution: A critical assessment of the harmonic approximation and the choice of the lineshape function |
| M. Carmen | Ruiz Delgado | 9 | Carbazole-based Diradicals for Dynamic Covalent Chemistry |
| Branislav | Milovanović | 10 | Alkali metal cations impact on the excited states properties of the guanine quartet |
| Claire | Tonnelé | 11 | (tentative) Nonlinear Optical Properties of Spirocyclohexadine Photochromes |
| Adam | Matěj | 12 | Tailoring π -conjugation and vibrational modes to steer onsurface synthesis of pentalene-bridged ladder polymers |
| Michal | Langer | 13 | Structural Dynamics of Carbon Dots in Water and N,N-Dimethylformamide Probed by All-Atom Molecular Dynamics Simulations |
| Marin | Sapunar | 14 | Wave function overlap based assignment of UV absorption spectra and state specific analysis of solvation effects |
| Tomislav | Piteša | 15 | Anti-Kasha nitrogen photoelimination from diazoalkanes |
| Ivan | Ljubić | 16 | Mechanisms and kinetics of free radical reactions in non-buffered and buffered aqueous solutions |