Ruđer Bošković Institute

11th – 13th December 2024

BOOK OF ABSTRACTS

“Hybrid modeling of (bio-)molecular multiscale phenomena”

2024

Zagreb, Croatia

IMPRESSUM

Workshop title: *“Hybrid modeling of (bio-)molecular multiscale phenomena”* (HYMO-M2P)

Dates: 11th – 13th December 2024

Venue:

Ruđer Bošković Institute (RBI)
Bijenička cesta 54,
10000 Zagreb, Croatia

Organizing Committee:

Dr. Antonio Prlj, Ruđer Bošković Institute
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We thank Ruđer Bošković Institute’s administration staff for the assistance.

Dear Friends and Colleagues,

We are pleased to welcome you to our small workshop on multiscale modeling of excitations in biological and functional molecular systems. Our aim was to organize an informal gathering of scientists working in the field of (bio-)molecular aggregates and assemblies, and more broadly (bio-)molecular materials, with a keen interest in excited states and excitons, optical properties and photophysics. This workshop provides an excellent opportunity to address recent advancements in theory and method development, as well as to bridge the gap between theory and experiment.

Thank you for joining us in Zagreb!

The Organizing Committee

Ruđer Bošković Institute

TABLE OF CONTENT

PROGRAM

Day 1 - Wed 11th December 2024

18:00	Get Together and Welcoming

Day 2 - Thr 12th December 2024 - RBI 1st Wing “Ivan Supek”

8:30	–	8:45	Registration
8:45	–	9:00	Opening
			Scientific Session 1 Chair: Luca Grisanti (CNR-IOM, RBI)
9:00	–	9:45	**IL1: Manas Panda** (online) Jadavpur University, Kolkata, India *“Bioinspired Smart Molecular Crystals for Actuation and Sensing”*
9:45	–	10:00	**CL1: Francesco Bertocchi** Università di Parma, Parma, Italy *“NIR optical nanothermometer based on organic radicals: monitoring temperature in biological tissues”*
10:00	–	10:30	*Coffee Break*
			Scientific Session 2 Chair: Tamara Rinkovec (RBI)
10:30	–	11:15	**IL2: Samuele Giannini** CNR - Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Pisa, Italy *“On the Role of Electronic Excitations and Vibronic Interactions in the Optical Properties and Dynamics of Organic Semiconductors for Photovoltaics”*
11:15	–	12:00	**IL3: Gabriele D'Avino** University of Venice, Venice, Italy Institut Néel, CNRS and Grenoble Alpes University, Grenoble, France *“Energy landscape of charge and energy carriers in complex molecular architectures: many body ab initio meets long-range electrostatics”*
12:00	–	12:15	**CL2: Filip Ivanovic** University College London, London, United Kingdom *“Nanoscale Non-adiabatic Dynamics Simulation of Charge Generation in Organic Solar Cells”*

12:15 – 12:30	**CL3: Marco Bardini** University of Mons, Mons, Belgium Institut Néel, CNRS, Grenoble, France *“Charge transport in novel record-mobility molecular semiconductors: cheap and accurate calculations with the “Phonomol” approach”*
12:30 – 14:00	*Lunch Break*

Day 2 - Thr 12th December 2024 - RBI 3rd Wing

	Scientific Session 3 Chair: Marin Sapunar (RBI)
14:00 – 14:45	**IL4: Anna Painelli** University of Parma, Parma, Italy *“Solid State Solvation”*
14:45 – 15:00	**CL4: Nađa Došlić** Ruđer Bošković Institute, Zagreb, Croatia *“When Theory Meets Experiment: Probing Ultrafast Electronic Relaxation in Uracil”*
15:00 – 15:45	**IL5: Federico Hernandez** University of Bristol, United Kingdom *“Multiscale methods to model photochemistry and photophysics in organic crystals”*
15:45 – 16:15	*Coffee Break*
	Scientific Session 4 Chair: Robert Vianello (RBI)
16:15 – 17:00	**IL6: Cristina Sissa** Department of Chemistry, Life Sciences and Environmental Sustainability, Parma, Italy *“Seeming and true violation of the Kasha's rule: unveiling the photophysics of multibranched dyes”*
17:00 – 17:15	**CL5: Marta Monti** The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy *“Exploring Non-Aromatic Luminescence through QM/MM Modeling for Bio-Compatible Materials”*
17:15 – 18:00	**IL7: Tomislav Piteša** Ruđer Bošković Institute, Zagreb, Croatia *“General Exciton-Based Approach to Describing the Electronic States of Multichrompohoric Systems”*
20:30	*Social Dinner*

Day 3 - Fri 13th December 2024 - RBI 3rd Wing

			Scientific Session 5 Chair: Dino Novko (Institute of Physics, Zagreb)
9:00	–	9:45	**IL8: Ganna Gryn'ova** Heidelberg Institute for Theoretical Studies, Heidelberg, Germany University of Birmingham, Birmingham, United Kingdom *“Multiscale Modelling and Design of Functional Organic Materials”*
9:45	–	10:00	**CL6: Ivor Lončarić** Ruđer Bošković Institute, Zagreb, Croatia *“Modeling molecular crystals with machine learning interatomic potentials”*
10:00	–	10:30	*Coffee Break*
			Scientific Session 6 Chair: Antonio Prlj (RBI)
10:30	–	11:15	**IL9: Laura Ratcliff** University of Bristol, Bristol, United Kingdom Hylleraas Centre for Quantum Molecular Sciences, Tromsø, Norway *“Simulating Disorder in Organic LEDs using Density Functional Theory”*
11:15	–	12:00	**IL10: Kun-Han Lin** National Tsing Hua University, Hsinchu, Taiwan *“Computational design of organic materials in optoelectronic applications”*
12:00	–	12:15	**CL7: Bernhard Kretz** Institut Ruđer Bošković, Zagreb, Croatia *“Predicting Electronic Properties of Nano-Porous Graphene with DFT and ML”*
12:15	–	12:30	**CL8: Bruno Mladineo** Institut Ruđer Bošković, Zagreb, Croatia *“A Machine Learning Approach to Study of Thermosalient Molecular Crystals”*
12:30	–	12:45	**CL9: Lorenzo Savi** University of Parma, Parma, Italy *“Charge and spin transport in chiral systems: a current-constrained approach”*
12:45	–	13:00	*Closing*

INVITED LECTURES

I1: Bioinspired Smart Molecular Crystals for Actuation and Sensing

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Nature provides numerous examples of smart systems that are smart and responsive to external stimuli or environmental cues. To mention a few examples, movement of sunflower plant under sunlight direction, pressure induced movements of mimosa pudica or venus flytrap, humidity and temperature induced flower blooming, self-healing of plant stem or human bone etc. These systems continue to inspire scientists to develop artificial materials that mimic such processes. For example, light-powered plants can autonomously change their shape, size or display static/ dynamic motion in presence of natural light/sunlight. Mimicking such functions in the laboratory, i.e developing light powered autonomous micro/macro-machines using soft organic/metal organic molecular material represents one of the most difficult challenges in today's research and demands huge imagination, skills, and tedious efforts from the involved researchers. Smart organic crystalline materials that can display macroscopic responses such as shape deformation, size alteration or motion under light illumination have emerged as potential candidates for this purpose. The design of such molecules is accomplished by incorporating a photo-active unit that can absorb photons to initiate photo-response and a suitable supramolecular synthon for non-covalent interactions for the propagation. On the simplest mechanistic view, the molecular motion triggered by light is cooperatively amplified to supramolecular to macroscopic scale with the help of intermolecular cooperative mechanism involving reconfigurable non-covalent interactions. While few such molecular crystals have been reported to exhibit fascinating macroscopic mechanical responses, the quest for developing new molecular systems having superior or novel mechanical responses is a never-ending process in material chemistry research. In this talk, we shall discuss some of the novel light responsive and self-healing materials that have recently been developed in our laboratory.

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2. S. Arivalagan, P. Giri, S. Richard, A. Husain, M. K. Panda, and G. C. Nandi, Crystal Growth & Design **24**, (2024).
3. P. Giri, A. Panda, and M. K. Panda, Chemistry – A European Journal **30**, (2024).
4. D. Dey, P. Giri, Nayim Sepay, A. Husain, and M. K. Panda, Journal of Photochemistry and Photobiology A: Chemistry **437**, 114480 (2022).
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I2: On the Role of Electronic Excitations and Vibronic Interactions in the Optical Properties and Dynamics of Organic Semiconductors for Photovoltaics

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Driven mainly by synthetic trial-and-error improvement, significant advancements have been made in the field of organic photovoltaics (OPVs), resulting in record-breaking power conversion efficiencies exceeding 19%. Organic molecular semiconductors like non-fullerene acceptors (NFAs) have been extensively used to accomplish this breakthrough. However, despite notable progress in refining the electronic and morphological aspects of these materials, systematic theoretical investigations into the photophysics of molecular aggregates remain relatively scarce. A fundamental understanding of the changes in optical properties upon aggregation and the establishment of structure-property relationships [1,2] could provide valuable insights for knowledge-driven advancements, potentially pushing the efficiency of these materials even further.

Here, I will discuss how first-principles-based model Hamiltonians, combined with quantum dynamics simulations performed using the multiconfiguration time-dependent Hartree (MCTDH) method—which accounts for non-adiabatic effects and couples electron-nuclear vibrations—enable the accurate reproduction of experimental optical properties in the investigated isolated molecules and related molecular aggregates. I will show how excitonic effects modify the shape of the spectral absorption upon aggregation and how intermolecular charge transfer states contribute to these differences by interacting with Frenkel-like excitations [2,3]. In closely interacting perylene-derivative systems, quantum dynamics simulations reveal ultrafast exciton transfer between monomers, occurring simultaneously with photo-induced charge transfer. Based on these simulations, I will propose strategies that leverage our understanding of how solid-state packing affects the properties of NFAs, with the aim of guiding intelligent material design to further enhance OPV performance.

References:

1. Giannini et al. Nat. Commun. (2022) 13, 2755
2. Giannini et al. Materials today (2024), 10.1016/j.mattod.2024.09.009
3. Giannini et al. J. Mat. Chem. C (2024), 12, 10009-10028

I3: Energy landscape of charge and energy carriers in complex molecular architectures: many body *ab initio* meets long-range electrostatics

Gabriele D'Avino[1,2*]

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The success of optoelectronic devices based on π-conjugated organic semiconductors relies on the possibility to carefully control the energy landscape of charge and energy carriers, as to drive their motion and ultimately achieve the desired functionality. The predictive character of theoretical simulations of electronic excitations in complex molecular systems hinges on the simultaneous presence of two factors, namely an accurate quantum framework for the electronic structure and a proper account of long-range interactions in the molecular environment. This lecture will offer an overview on our recent work on the multiscale, QM/MM, modelling of electronic excitations in molecular solids, based on many-body perturbation theories (GW and Bethe-Salpeter formalisms) and classical techniques for electrostatic and dielectric embedding. After giving a brief overview of the methodology, I will cover selected case studies, in which theoretical calculations enabled by a precise knowledge of the supramolecular organization allowed to rationalize intriguing observations in photoemission and optical spectroscopies, shedding light on fundamental mechanisms of great potential for application in photovoltaics and doped semiconductors. Finally, I will present a novel diabatization scheme that enables the systematic mapping of many-body QM/MM calculations to few-state models for the accurate, insightful and computationally-cheap study of excitons in large supramolecular architectures.

References:

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I4: Solid State Solvation

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The efficiency of organic optoelectronic devices relies on the careful optimization of the active dye in its local surrounding, making solid state solvation (SSS) a powerful, but poorly understood and exploited, materials design tool. Comparing Raman or absorption spectra of a small rigid polar dye (like e.g. Nile red) dispersed in an amorphous matrix with the spectra of the same dye dissolved in liquid solvents gives reliable information of the equilibrium dielectric properties the matrix. But SSS has more important and tricky effects on emission spectra, since dielectric relaxation occurs in matrices on similar timescales as emission processes. We present unprecedented information on the dielectric dynamics of mCBPCN and DPEPO matrices, commonly used in OLEDs, obtained from the analysis of time-resolved emission spectra of Nile red, collected in a wide time window (15 fs - 15 ns). The dielectric relaxation, responsible for a sizable dynamical red-shift, is characterized by matrix-dependent timescales, extracted via a detailed theoretical analysis. The proposed approach to static and dynamic dielectric behavior is easily applicable to any amorphous material. These results shed new light on the emission properties of dyes in amorphous matrices, an issue of enormous interest for OLED. [1]

References:

1. Brunella Bardi, Davide Giavazzi, Elena Ferrari, Alessandro Iagatti, Mariangela Di Donato, D. K. Andrea Phan Huu, Francesco Di Maiolo, Cristina Sissa, Matteo Masino, Andrea Lapini, Anna Painelli, *Mater. Horiz.* **10**, 4172–4182 (2023).

I5: Multiscale methods to model photochemistry and photophysics in organic crystals

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Light-activated phenomena underpin applications in energy and optoelectronic materials. These processes occur in the condensed phase, where the environment plays an active role, either by restricting the motion of the excited molecules or directly participating in the main excited-state mechanisms [1]. A full understanding of these phenomena at the atomic level is essential for optimizing quantum efficiencies and aiding the design of new materials with tailored properties. Excited state calculations, particularly excited state dynamics, provides an insightful picture of light-activated processes at the intra- and intermolecular levels. However, computational studies of photophysics and photochemistry in the solid state are extremely challenging due to the substantial computational cost of high-fidelity calculations for chromophore excited-state dynamics in periodic systems.

In this talk, I will show how multiscale approaches, combining QM/QM’ electrostatic embedding schemes in the static and in the dynamic frameworks, enable accurate modelling of excited state mechanisms driving to interesting photochemistry and photophysics in molecular crystals [2]-[5]. Additionally, I will show how this scheme can be used to train machine learning models, making it possible to solve the photodynamics of systems that are intractable at the QM level, enabling fully atomistic excited-state dynamics for the solid state with multiconfigurational quantum mechanical calculations [5].

References:

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[2] F. J. Hernández and R. Crespo-Otero. J. Mat, Chem, C, 2021, 9, 11882
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I6: Seeming and true violation of the Kasha's rule: unveiling the photophysics of multibranched dyes

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Kasha's rule, a foundational principle in molecular spectroscopy, states that fluorescence arises from the lowest-energy excited state with the same spin multiplicity as the ground state. For fluorescence to occur, this lowest excited state must be a bright state with a significant transition dipole moment. Kasha's rule is an empirical principle relying on the fast relaxation of an excited molecule toward the lowest excited state (in the same spin manifold). This internal conversion typically occurs in ~ 10^{-12} seconds. Accordingly, emission (typically occurring in the ns time window) is only observed from the lowest excited state, the so-called Kasha's state. While not an exact law, the validity of the Kasha's rule is fairly general, and the few exceptions are noteworthy, and deserve attention to shed light on the mechanisms of excited-state reactions.

This study aims to explore the seeming and true violations of Kasha's rule in multibranched molecular systems, focusing on the phenomena of excited-state symmetry breaking and the emergence of low-lying dark states that disrupt the conventional understanding of fluorescence. We present a detailed investigation of phenyleneethynylenes and rhodanine-based organic dyes, using a combination of experimental techniques and quantum chemical calculations. In the case of phenyleneethynylenes, we show that large Stokes shifts and intense fluorescence emission are observed despite the presence of low-energy dark states. The seeming violation of the Kasha's rule is explained by a novel mechanism termed "symmetry swap," where the energy order of excited states is inverted due to symmetry breaking.[1] For the rhodanine-based dye, we observed a marked increase in fluorescence intensity at low temperatures, alongside a surprising wavelength-dependent fluorescence quantum yield, which is inconsistent with the Kasha's rule. Experimental results are rationalized in terms of a temperature-dependent violation of the Kasha's rule.[2]

These findings indicate that in both cases, the photophysical properties are governed by complex relaxation pathways and the influence of low-lying dark states, highlighting the need for a detailed characterization of excited-state dynamics in multibranched dyes.

References:

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2. O. Racchi, S. Scurti, S. Liotino, A. Lanfranchi, A. Painelli, D. Comoretto, D. Carretti, C. Sissa, *paper in preparation*

I7: General Exciton-Based Approach to Describing the Electronic States of Multichrompohoric Systems

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Nowadays there is a versatile variety of accurate electronic-structure methods for the excited-state calculations, such as TD-DFT, MP/ADC, EOM-CC, CASPT2, MRCI etc. However, all of these methods scale unfavorably with the system size, and therefore are often not applicable on large systems, such as multichromophoric ones. An alternative to the direct treatment of the full system in these cases is to employ an excitonic model. The underlying philosophy of all excitonic models is to obtain the electronic states of individual chromophores (site states), and then construct a set of their antisymmetrized products (excitonic basis). The full-system Hamiltonian is then represented in the excitonic basis and diagonalized [1]. Many of the so-far developed models rely on the famous Frenkel excitonic model, which employs an *ad hoc* parametrization the Hamiltonian in the basis of only local-excitation products – ones having only one site in an excited state [2,3].

In this talk I will present the Excitonic Configuration Interaction (ECI) method – an excitonic-like approach which (i) self-consistently constructs the excitonic basis so that it minimizes the full-system ground-state energy, (ii) can account for the contributions of both local and multi-local excitations, as well as the charge-transfer configurations, to the full-system states, and (iii) builds the exciton Hamiltonian independently of the method employed in the site-state calculations. The performance of ECI, as well as its comparison with the Frenkel model, will be illustrated on an array of testing examples of multichromophoric systems.

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I8: Multiscale Modelling and Design of Functional Organic Materials

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Functional, topologically complex organic molecules are rising stars in modern materials science due to their biocompatibility, structural variability, and wealth of physico-chemical properties. Their practical applications often involve interactions with small molecular targets (e.g., gases, environmental pollutants, and drugs) *via* relatively weak non-covalent forces. Key to these interactions are the diverse physico-chemical features of host materials: arrangement of functional groups, availability of pores and cavities, conductivity, etc.

In this contribution, we will discuss our efforts towards rational design of graphene-based materials for applications in sensing and electrochemistry. Infinite structural variety and a broad range of sizes of graphene-based materials (GBMs) and their molecular (nano-) variants challenge the computer-aided design of these systems for specific sensing applications [1]. We demonstrate how the choice of *in silico* model and of the level of theory influence computed properties of GBMs, from adsorption energetics to redox transformations. We also illustrate how the properties of an "infinite" material can be extrapolated from high-level computations on finite nanoflakes. Finally, we discuss the dependence of the redox and adsorbent properties of GBMs on their sizes and functionalisations, providing guidelines for a targeted design of graphene-based sensors.

References:

1. A. Piras, C. Ehlert, G. Gryn'ova. *WIREs Comput. Molec. Sci.* **11**, e1526 (2021).

I9: Simulating Disorder in Organic LEDs using Density Functional Theory

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Organic semiconductors have favourable properties for use in devices such as organic light emitting diodes (OLEDs), including low cost and light weight. The current generation of OLEDs are based on molecules containing heavy metals, motivating the use of purely organic molecules exhibiting thermally activated delayed fluorescence (TADF) for efficient and environmentally-friendly devices. A key property for TADF is a small singlet-triplet splitting, which, like ground state properties, can be strongly influenced by both the internal disorder and that of the surrounding environment. The effects of this disorder can be probed through density functional theory (DFT) simulations of large enough systems to study explicit environmental effects, which can necessitate new methods which are capable of treating large systems, while maintaining a high enough accuracy for both ground and excited state properties. This has motivated the development of a new method, named transition-based constrained DFT (T-CDFT), which aims to treat excited states in large systems and has been implemented within a linear scaling DFT framework. In this talk I will introduce T-CDFT[1], and show how it may be used in conjunction with other DFT-based approaches to explore disorder in core, valence and excited states, focusing on the prototypical TADF emitter 2CzPN[2].

References:

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2. N. K. Fernando, M. Stella, W. Dawson, T. Nakajima, L. Genovese, A. Regoutz, and L. E. Ratcliff, *Phys. Chem. Chem. Phys.* **24**, 23329 (2022)

I10: Computational design of organic materials in optoelectronic applications

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In recent years, organic light-emitting diodes (OLEDs) have become a key player within the display and lighting industry. Despite these increasing demands in OLEDs, several barriers remain to be overcome to achieve high-performance, cost-effective, and long-lifetime blue OLEDs. One of the challenges comes from the material side, where the lifetime and the efficiency roll-off of blue OLEDs are expected to be further improved if ideal organic emitters and organic host materials can be found. In this study, we address this challenge through three strategies.

To gain insights into designing stable and high-performance host materials, we investigated the structure–packing–mobility relationship in pure hydrocarbon host materials using a multiscale approach. Our analysis of spirobifluorene (SBF) dimers, which differ only in the substituent position linking two SBF units, underscores the critical role of substituent position in determining charge carrier mobility. The observed differences in transport properties primarily arise from variations in the reorganization energy associated with electron transfer.

In addition, we addressed the need for stable and efficient blue emitters by performing high-throughput screening on a library of over 4,000 molecules featuring a space-confined charge transfer (SCCT) design. Using an automated workflow, we identified several promising compounds with potential as high-performance blue emitters. Our results highlight the importance of carefully selecting computational functionals to accurately predict excited-state energies.

Finally, recognizing that thermal stability is a key requirement for organic thin films, we developed a fast and reliable computational protocol for predicting glass transition temperature (T_g). By integrating a semi-automated force-field parameterization tool with a molecular dynamics simulation protocol, we significantly reduced both human effort and computational cost associated with T_g prediction. Together, these strategies provide a comprehensive framework for advancing the development of high-performance OLED materials.

CONTRIBUTED TALKS

C1: NIR optical nanothermometer based on organic radicals: monitoring temperature in biological tissues

Francesco Bertocchi[1*], Nerea González Pato[2], Davide Blasi[2], Domna N. Nikolaoidou[1], Jesus Cerdá[3], Andrea Lapini[1], Francesca Terenziani[1], Nora Ventosa[2], Juan Aragó[3], Jaume Veciana[2], Imma Ratera[2]

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Accurate measurement of the local temperature of tissues and cell cultures is essential for understanding biological processes. NIR-to-NIR chromophores (i.e. chromophores which absorb and emit radiation in the NIR spectral range) have emerged as powerful spectroscopic probes for non-invasive temperature sensing due to the deep penetration of NIR radiation into biological tissues. Two-Photon Absorption (TPA) microscopy guarantees reduced photobleaching and intrinsic three-dimensional resolution. We report the preparation and spectroscopic characterization of photostable organic nanoparticles (ONPs) of TTM-αH doped with a polychlorinated trityl radical, TTM.[1] TTM radicals exist either as isolated radicals or form excimers within the ONPs. The excimers can be two-photon excited, potentially working as promising NIR-to-NIR optical probes. The ratio between the intensities of monomer and excimer emissions significantly increases with increasing temperature.[2] This allows to reliably monitor temperature changes of a sample in a range between 278 and 328 K. The ratio of excimer to monomer emission is monitored both in an ONP water suspension (upon linear and two-photon excitation) and in an enucleated pig eye sclera (via two-photon microscopy), showing an excellent linear correlation with temperature and thus demonstrating the potential of TTM ONPs as nanothermometers for biological applications.[3]

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C2: Nanoscale Non-adiabatic Dynamics Simulation of Charge Generation in Organic Solar Cells

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In organic solar cells (OSCs), excitation by light yields a tightly bound electron-hole pair, termed an exciton, which can dissociate into free charges. OSCs' pi-conjugated molecular constituents can allow fast exciton and charge transport, and can be easily tuned to optimise their properties relevant to charge generation, such as bandgap and interface structure. Along with their underlying materials' typical abundance and ease of processing, OSCs suggest a viable alternative or supporting role to their inorganic counterparts.

Two-component cells, where two species are separated by an interface, constitute OSCs' greatest leap towards commercialisation, with their highest efficiencies exceeding 19%. Although such an interface is crucial for the dissociation of excitons, understanding the exact mechanism by which free charges are generated across the interface remains a formidable theoretical challenge, with contradictory results having been reported in the literature[1]. The complexity of such systems precludes a complete treatment by analytical theories, and instead requires first-principles quantum dynamics simulations, which must also be fast enough to access time scales comparable to experiment.

Here, we use an in-house non-adiabatic molecular dynamics package, termed X-SH[2], to simulate charge generation in an oligothiophene-perylene diimide interface, on experimentally relevant time and length scales. Our use of a DFT-parameterised Hamiltonian, which is updated on-the-fly, bypasses the need for explicit electronic structure calculations during the dynamics.

We elucidate the mechanism of charge generation in such an interface by modelling the excitons and charges with an explicit electronic wavefunction. This allows us to track their locations in real-time, on a microscopic scale that often cannot be resolved with photochemical experiments. We leverage the computational speed and flexibility of X-SH to identify key physical parameters affecting the efficiency of charge generation, and translate this into design rules to guide the synthesis of OSCs with yet higher efficiencies.

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C3: Charge transport in novel record-mobility molecular semiconductors: cheap and accurate calculations with the “Phonomol” approach

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The study of crystalline organic semiconductors (OSCs) includes several families of compounds, such as NDIs, acenes, thienoacenes, and others. Recently, a novel pyrene derivative broke the long-standing record for charge mobility previously held by rubrene, featuring mobility as high as 30 cm^2/Vs, opening new pathways in materials design [1]. Varied modeling techniques have been applied to tackle phonons and charge transport in these materials [2] [3]. Ab-initio density functional theory (DFT) with a plane-wave basis offer a reliable framework for computing harmonic lattice dynamics. This, however, comes at a huge computational cost, especially when supercells are needed to sample lattice motion throughout the Brillouin zone. The Phonomol method greatly speeds up the calculation of harmonic frequencies in these crystals, exploiting the molecular nature of OSCs. Phonomol implements a finite-displacement, frozen-phonon, method based on plane-wave DFT, employing molecular displacements instead of atomic ones. Expensive crystal-phase calculations for displacements are explicitly performed only for low-frequency molecular motions, while those concerning high-frequency modes are avoided and safely approximated from molecular gas-phase calculations. This method makes it possible to compute the full vibrational spectrum (i.e. including Brillouin zone sampling and full mode mixing) with great accuracy at an affordable computational cost for several organic crystals. Phonon calculations and the ensuing electron-phonon analysis provide the parameters for computing charge mobility within the framework of transient localization theory. In this talk, we will present the Phonomol method and then show its application to study charge transport in both well-known (e.g. DNTT [4]) and novel (pyrene) OSCs. Our analysis sheds light onto the unprecedented transport properties of the new material, unveiling limits and opportunities for further material optimization.

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C4: When Theory Meets Experiment: Probing Ultrafast Electronic Relaxation in Uracil

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Trajectory surface hopping simulations have become increasingly prominent in computational spectroscopy. The development of efficient techniques for calculating photoelectron spectroscopy observables, along with the creation of trajectory-based protocols for simulating photoelectron spectroscopy signals, has significantly enhanced our ability to track excited-state dynamics with remarkable efficiency. In this talk, I will outline a computational strategy for simulating time-resolved photoelectron spectra focusing on a recent application that provides detailed insights into the photoinduced dynamics of uracil.

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C5: Exploring Non-Aromatic Luminescence through QM/MM Modeling for Bio-Compatible Materials

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Luminescence in biological systems is typically attributed to the presence of aromatic or conjugated groups. [1] However, recent studies have shown that peptide or single amino acid aggregates can emit visible light even in the absence of these moieties. [2,3] This behavior is particularly intrguing given that some of these protein aggregates are implicated in the development of neurodegenerative diseases. [4] Therefore, this phenomenon has sparked interest across various fields, as it suggests that electronic interactions between non-optically active molecules can lead to fluorescent supramolecular assemblies. Elucidating the mechanism behind this fluorescence is essential for a variety of applications, ranging from early disease detection to the engineering of novel biophotonic materials. In order to investigate the excited state dynamics of these materials, we employ the trajectory surface-hopping method, using the time-dependent density functional theory to describe the electronic structure. [5] A quantum mechanic/molecular mechanic (QM/MM) approach is utilized to model the peptide (or amino acid) crystal of interest to achieve a good compromise between accuracy and computational cost. [6] In collaboration with experimental groups, we are currently investigating how factors such as solvent, crystal packing, or protonation state may influence the luminescence of amino acid-based solid materials.

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C6: Modeling molecular crystals with machine learning interatomic potentials

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Molecular crystals are a common and important class of crystalline materials. However, modelling molecular crystals based on first principles (eg. with density functional theory) is often difficult due to the size of a typical unit cell. Therefore, high-throughput calculations for the discovery of useful properties are rare. In this presentation, I will show how machine-learned interatomic potentials can enable accurate and fast calculations of mechanical and thermal properties of molecular crystals [1,2] enabling an understanding of experimental observations as well as high-throughput search for materials with the desired properties[3]. In principle, to train machine learning potential one would need to create a sufficiently large database of molecular crystals calculated with the desired accuracy. This is also a very challenging task and we will show how to avoid this step using transfer learning and existing databases of small systems.

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C7: Predicting Electronic Properties of Nano-Porous Graphene with DFT and ML

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Nano-porous graphene (NPG) has emerged as a promising material due to its tunable electronic properties. Specifically, by modifying structural parameters, the band gap can be tuned over a wide range of values[1,2], from metallic structures to semiconductors. This opens up exciting possibilities for applications in electronics such as field-effect transistors. However, due to limitations in experimental and computational throughput, a comprehensive understanding of the relationship between NPG's structure and its resulting properties remains elusive.

This work combines density functional theory (DFT) with modern machine learning (ML) methods to systematically investigate both static and dynamic electronic properties across a set of 460 NPG structures derived from four distinct templates. DFT calculations reveal relationships between structural parameters and band gaps within subsets of our NPG structures, offering valuable insights for semiconductor applications. Notably, we discover that certain NPG configurations exhibit band gap behavior analogous to armchair graphene nano-ribbons.

Based on our DFT results, we trained two distinct neural networks: one to predict forces and total energies, and another one to predict band gaps. By combining these networks, we perform molecular dynamics simulations at different temperatures for all 460 NPG structures, enabling us to predict band gaps under different operating conditions. This temperature-dependent analysis of the band gap is important for semiconductor applications, as elevated temperatures may cause a material to transition from a semiconductor to a conductor. Our findings identify several NPG structures with band gaps suitable for semiconductor applications and sufficient temperature stability to function effectively within the typical operating temperatures of semiconductor devices.

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C8: A Machine Learning Approach to Study of Thermosalient Molecular Crystals

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Thermosalient materials change size dramatically when heated or cooled. Their crystals go through a rapid and energetic transition where they jump to distances much bigger than their original size.

The computational study of the thermosalient effect in materials requires a high level of accuracy that can only be achieved through ab-initio techniques such as DFT. However, accurately simulating systems of this size demands a lot of computational power, which makes such calculations impractical. Fortunately, recent developments in machine learning, specifically equivariant graph neural networks [1] make it possible to create accurate machine learning interatomic potentials (MLIPs) efficiently. In this way, we can approach the accuracy level of DFT while benefiting from linear scaling akin to classical potentials.

Starting with just three experimental structures that represent the phases of the molecular crystal, an efficient and versatile dataset was created using normal mode sampling and then further improved using active learning. After reaching the plateau in the improvement of the potential this MLIP was used for calculations of free energy using the harmonic approximation and quasi-harmonic approximation. This way we can explain experimentally observed phase transitions and gain a better understanding of thermosalience.

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C9: Charge and spin transport in chiral systems: a current-constrained approach

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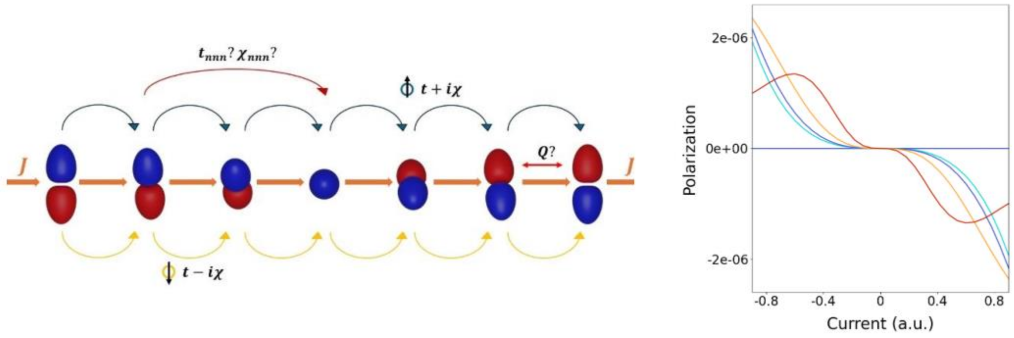
Chirality-induced spin selectivity (CISS) indicates a wide variety of phenomena occurring in chiral media, where the spin orientation of an electron affects its behavior. CISS was first observed, [1] more than 30 years ago, in photoemission experiments that revealed significant asymmetry in scattering probabilities as spin-polarized electrons were driven through a thin layer of chiral molecules. Nowadays, various experiments have demonstrated remarkable efficiency in spin filtration, even at the single-molecule level[2] Driven by the potential for applications in fields such as quantum technologies, spintronics, and enantioselective chemistry, tremendous efforts have been devoted to elucidate the mechanism behind CISS, without reaching a quantitative agreement with experiments. In this work, we investigate CISS in electron transport, relying on a modified Hubbard model to include spin-orbit coupling (SOC). Specifically, current is driven through the system via the current-constrained approach to achieve a steady-state condition where spin current and spin polarization can be directly observed. We analyze the role of the connectivity among the sites, of vibrational degrees of freedom as well as of two-electron terms in the SOC operator, beyond the standard mean-field approximation.



Scheme of the systems and preliminary results. Left: a chain of twisted p orbitals, linked by nearest-neighbors hopping and SOC term. The role of connectivity, vibrations, and bielectronic terms is questioned. Right: spin polarization against the imposed current for some sets of parameters.

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