Marie Skłodowska-Curie Innovative Training Network

HORATES

NEWSLETTER #**3** 2023

Hybrid and **OR**g**A**nic **T**hermo**E**lectric **S**ystems

The ongoing development of the **internet of things** (IoT) leads to completely new opportunities for **thermoelectric generators** based on **organic and hybrid materials**.

Our **mission** is to **train young professionals** that will be able to operate into this highly interdisciplinary field.

HORATES training will develop along three main guidelines:

Acquiring solid background in different **scientific and technological fields**, all related to hybrid and organic thermoelectrics;

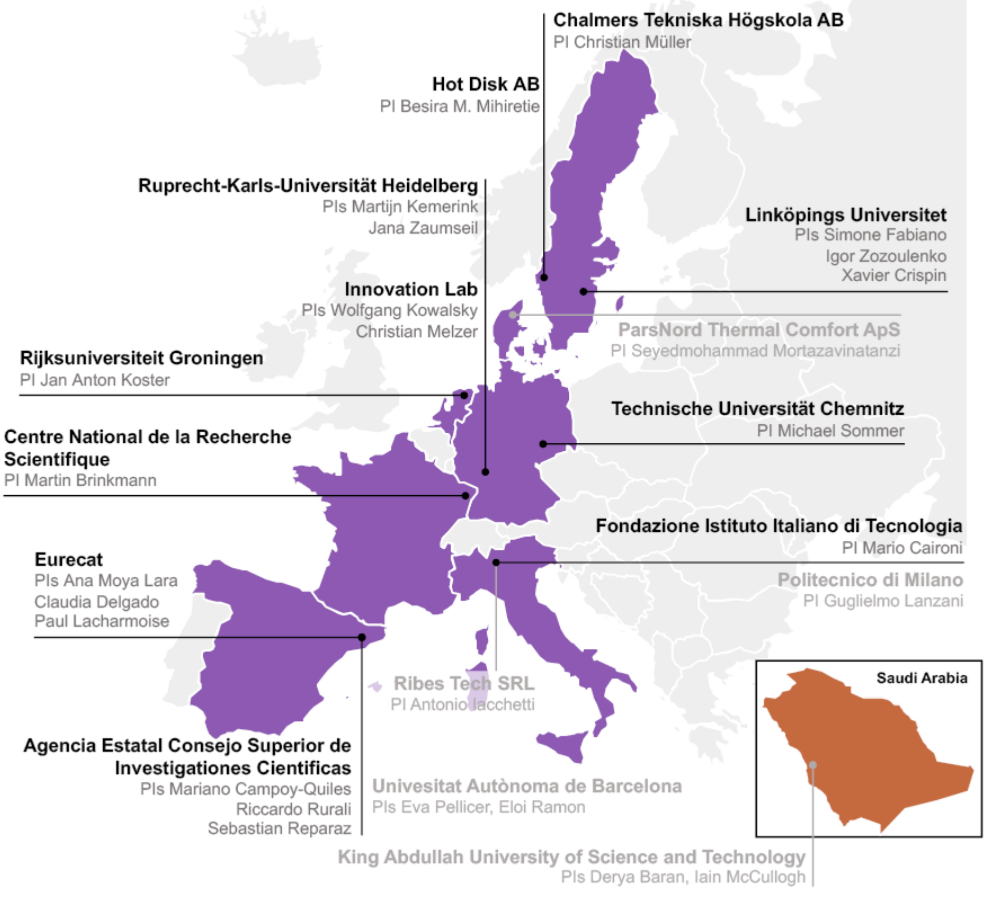
Exposing HORATES ESRs to **diverse sectors**, such as academia, technological research centers and industrial nodes;

Fostering the development of **transversal competencies**.

HORATES Mission

HORATES is a **Marie Skłodowska-Curie Innovative Training Network** (MSCA-ITN-ETN) aiming to train the **next generation of R&D innovators in hybrid and organic thermoelectrics** and develop prototype energy harvesters inspired by actual market demand.

The HORATES consortium:



11 Beneficiaries and **5 associate partners** from **7 European countries** and **1 non-European country**. This consortium brings together expertise from academic and non-academic nodes to ensure the **15 ESRs** are exposed to a real multisectoral exposure.

This project has received funding from the European Union's Horizon 2020 research and programme under the Marie Sklodowska-Curie grant agreement no. 955837

MARIE CURIE ACTIONS

Marie Skłodowska-Curie Innovative Training Network

HORATES in numbers:

MEETINGS

- 1 kick-off meeting
- 5 network meetings already implemented
- 5 training workshops already implemented
- 1 organized Symposium of the EMRS in Strasbourg

DISSEMINATION & COMMUNICATION

- **33** papers with ESRs and PIs as the co-authors already been published and many others are under review or in preparation
- **68** oral/poster presentations at conferences and seminars
- **8** conferences/workshops organized

INTERACTIONS

- 1 graduate summer school attended
- 2 trade fairs attended
- 38 training activities implemented

ESRs visiting IIT in Milan (Italy)

Related training and dissemination activities

Webinars of the courses given by PIs
https://horates.eu/publications/

Michael Sommer
Synthesis and characterization of conjugated polymers exemplified by naphthalene diimide bithiophenecopolymers (PNDIT2)
Video

Igor Zozoulenko
Conducting polymers for thermoelectric applications: electronic, transport and thermoelectric properties
Video

Martin Brinkmann
Investigating the structure and morphology in polymer semiconductors by transmission electron microscopy
Video 1 Video 2

Mario Caironi
Introduction to printed electronics and printed OTEGs
Video

Martijn Kemerink
The Peer-Review Process
Video

Mariano Campoy-Quiles
High throughput screening of materials
Video

Riccardo Rurali
Fundamentals of heat transport, basic ideas, different transport regimes, role of interfaces (boundary resistance, nanowires, etc)

Sebastian Reparaz
State of the art techniques to measure thermal properties
Video

Mariano Campoy-Quiles
Thermal conductivity of polymers

Training workshops & schools

The HORATES Network offers a wide range of training opportunities to its ESRs, including 5 international schools on more specific scientific topics and 5 workshops on complementary and transferrable skills.

Workshops and international schools held in **2023** and upcoming for **2024**:

International School 4:
Advanced Topics in OTE;

Workshop 4: *From the initial idea to market entry*

International School 5: *Printed Electronics and Opportunities for OTE;*

Workshop 5: *Career Development, incl. Postdoc Funding*

International conference organized by HORATES PIs

E-MRS Symposium T
Strasbourg, ***27-31 May 2024***

Doping in organic semiconductors: fundamentals, materials and applications

Special focus on :
- *Synthesis*
- *Processing and Characterization*
- *Upscaling and Devices*
- *Theory and Modeling*

Organizers: J.A. Koster, M. Caironi, M. Kemerink, and S. Sergi-Galindo

https://www.european-mrs.com/doping-organic-semiconductors-fundamentals-materials-and-applications-emrs

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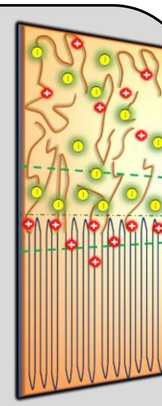
MARIE CURIE ACTIONS

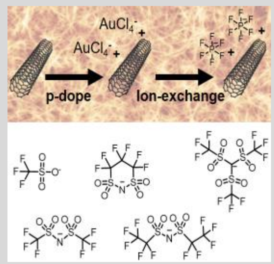
The ESRs' scientific achievements thus far:

Aditya Dash (ESR1, Universität Heidelberg, Germany):
The possibility to control the charge carrier density through doping is one of the defining properties of semiconductors. For organic semiconductors, the doping process is known to come with several problems associated with the dopant compromising the charge carrier mobility by deteriorating the host morphology and/or introducing Coulomb traps. For inorganic semiconductors these factors are mitigated through (top-down) modulation doping, a concept not yet employed in organics. In collaboration with S. Guchait (ESR12), we show that properly chosen host/dopant combinations can give rise to spontaneous, bottom-up modulation doping, in which the dopants preferentially sits in an amorphous phase, while the actual charge transport occurs predominantly in a crystalline phase with an unaltered microstructure, spatially separating dopants and mobile charges. Combining experiments and numerical simulations, this work shows that this leads to exceptionally high conductivities at relatively low dopant concentrations (DOI: 10.1002/adma.202311303.)



Amorphous/crystalline Junction

Angus Hawkey (ESR2, Heidelberg University, Germany):
I am investigating the role of dopant counterions on the thermoelectric properties of polymer-wrapped single-walled carbon nanotubes (SWCNTs). To achieve this, I have fabricated dense films of purely semiconducting SWCNTs and p-doped them by ion-exchange doping to exchange the dopant counterion with anions of varying size. At the same charge carrier density, we observe changes to the thermoelectric properties with ion size. In collaboration with Aditya Dash (ESR1), we aim to understand the reasons for these changes using his model for the thermoelectric properties of SWCNTs.



Doping strategy of semiconducting SWCNTs

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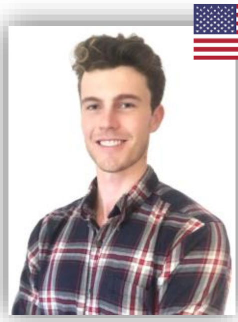
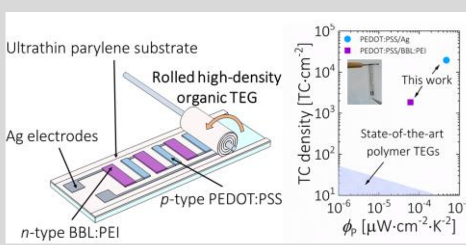
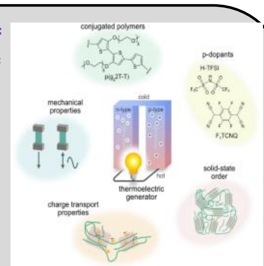


Nathan James Pataki (ESR3, Istituto Italiano di Tecnologia, Italy): I have been working on the design, fabrication and characterization of organic thermoelectric generators (TEG) using organic semiconducting materials from within the HORATES ITN. Our recent work, soon to be published in Advanced Functional Materials, presents a rolled, organic μTEG architecture combining large-area, solution-based deposition techniques, and an ultrathin parylene substrate to achieve a record thermocouple density of 1842 TCs·cm-2 and a conversion performance of 0.15 μW cm-2 at ΔT = 50 K.



Rolled high-density TEG architecture and properties

Mariavittoria Craighero (ESR4, Chalmers University of Technology, Sweden): I work on the processing and doping of p-type conjugated polymers for thermoelectrics. So far, I have studied the structure-property relationship with regard to thermoelectric and mechanical properties of p-doped oligoether substituted polythiophenes. I investigated the impact of of chemical doping and side-chain length on the nanostructure of thin films and how these affect the final electrical conductivity and thermoelectric performance of the material.



Furthermore, the mechanical robustness and flexibility of free-standing films of the p-doped polythiophenes have been studied and how they are affected by chemical doping. In collaboration with Joost Kimpel (ESR5), I am exploring the doping efficiency of novel thieno[3,2-b]thiophene polymers. With Qifan Li (ESR8), I am working on n-type yarns for thermolectric textiles. (DOI: 10.1021/acsaelm.3c00936)

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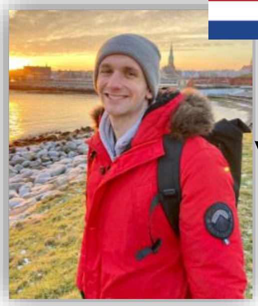
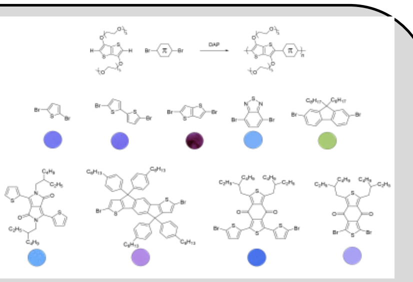


Joost Kimpel (ESR5, Chalmers University of Technology, Sweden): Many polymers that are currently explored in the context of organic thermoelectrics suffer from a too high scientific complexity index, which complicates upscaling. Direct arylation polymerization (DAP) of a series of conjugated polymers comprised of a thienothiophene-based monomer has been, which combine a low synthetic complexity index with a promising thermoelectric and electrochemical performance.



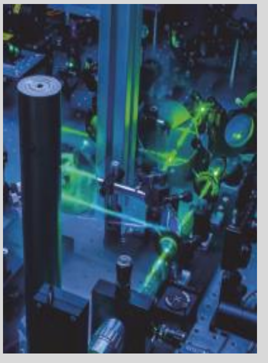
A thieno[3,2-b]thiophene-based monomer is utilized, which possesses only two activated C-H positions due to functionalization with oligoether side chains, which leads to highly regular polymers with high molecular weights. Combination of g_3TT with a wide range of common conjugated comonomers has been done, including electron-rich, electron-deficient, and neutral comonomers. Several of the newly synthesized polymers feature a promising electrical conductivity upon chemical doping, as well as a high transconductance in organic electrochemical transistors.

Jiali Guo (ESR6, Institute of Materials Science of Barcelona, Spain):

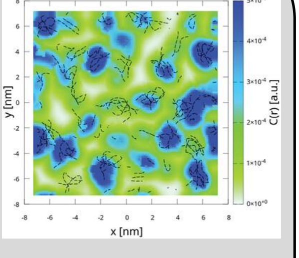
The study of in-plane thermal transport in bulk and low dimensional anisotropic materials is going to be crucial in next years as these materials are incorporated in applications such as electronics, thermoelectrics, and heat management devices.

The current devices and methods are complex, and may be influenced by the shape of the heat source and/or are mostly suitable for electrically insulating samples.

We present a new contactless device and method for studying thermal transport with enhanced sensitivity to in-plane heat conduction, which is based on beam-offset frequency-domain thermoreflectance using a one-dimensional heat source with uniform power distribution (DOI: 10.1016/j.ijheatmasstransfer.2023.124376). The method has been validated for free standing films, bulk samples (e.g. anisotropic crystals and substrates) and thin films on a substrate, including neat and doped conjugated polymers used for thermoelectrics.



Paolo Sebastiano Floris (ESR7, ICMAB, Spain): I have investigated the influence of doping on the lattice thermal conductivity of PEDOT, while varying the chain length distribution and using either an atomic (Cl) or a large polymeric anion (PSS). I found that longer chain lengths result in higher conductivities when the polymer is undoped, whereas intermediate chain lenghts (10 - 12 monomers) give the highest thermal conductivities when doping is considered. This difference in behavior is linked to the different relationship between chain length distribution and mass density in the two states, which arises from the aromatic to quinoid transition that PEDOT undergoes upon doping (DOI: 10.1002/adfm.202215125).



Charge doping is responsible for an overall increase in thermal conductivity and for the reduction in the characteristic π-π distance from 4 to 3.6 Å. Finally, I found that PSS increases the thermal conductivity due to its intrinsically better transport properties.

Qifan Li (ESR8, Linköping University, Sweden): My project aims to investigate the newly discovered dopant-free high-conductivity polymeric systems based on ground-state electron transfer, synthesizing new conductive n-type conjugated polymers and investigate their ink formulation. So far, we submitted a paper titled "A Rolled Organic Thermoelectric Generator with High Thermocouple Density" in collaboration with Nathan James Pataki (ESR 3) and Najmeh Zahabi (ESR 9). Furthermore, we present a novel synthesis method enabling direct polymerization in water, yielding a highly conductive, water-processable n-type conjugated polymer, with remarkable electrical conductivity as high as 66 S cm^{-1}, ranking among the highest for n-type polymers processed using green solvents (paper in preparation).

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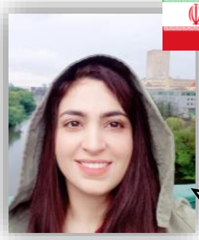
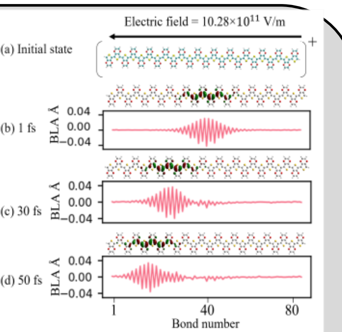


Najmeh Zahabi (ESR9, Linköping University, Sweden):

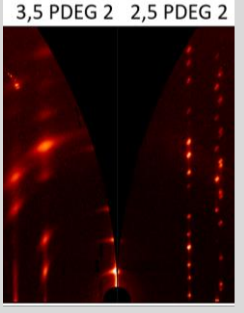
We have developed a computational technique based on ab initio Car-Parrinello molecular dynamics to investigate the temporal motion of charge carriers in the archetypical conducting polymer PEDOT. To achieve this, we monitor bond length alternations and charge density distribution induced by polaron motion in both a single PEDOT chain and in π-π stacked chains. For detailed information and results, please refer to our paper at https://doi.org/10.1063/5.0169363. In another study, we employed the atom-centered density matrix propagation method to gain microscopic insights into the charge carrier's dynamic in PEDOT, focusing on the effect of the electric field, temperature, and (deep and shallow) trapping by dopants. (under submission)

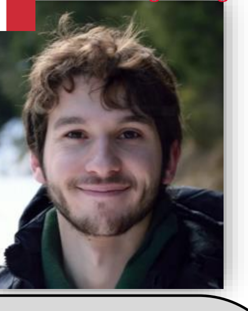


Dynamic evolution of polaron in PEDOT chain with N = 24 monomers subjected to the E = 10.28×10^{11} V/m electric field force. (a) shows a schematic representation of the geometrical structure of the PEDOT chain with N = 24 monomers, in the presence of a positive charge and an E = 10.28×10^{11} V/m electric field force. The upper panels in (b)-(d) depict the charge density distribution of the polaronic state. Red lines in (b)-(d) represent the bond length alternation at selected times.

Federico Ferrari (ESR10, University of Groningen, The Netherlands):

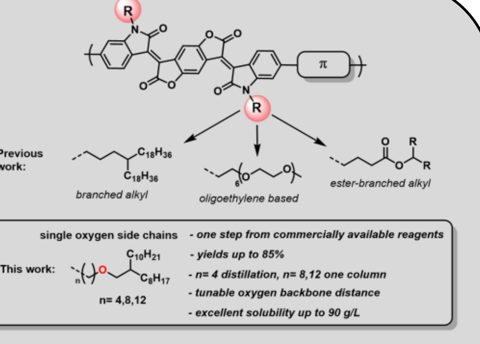
In the past year, I delved deeper into the influence of regiochemistry on the structure and thermoelectric properties of fullerene derivatives. By combining X-ray diffraction techniques from our colleagues in KAUST and solid-state devices we have come to understand how changing the orientation of a glycol chain can tremendously improve the thermoelectric performances of organic semiconductors.





Diego Ropero Hinojosa (ESR11, TU Chemnitz, Germany):

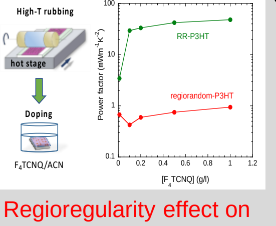
We have investigated the impact of side chain synthesis and length variations on the properties of single oxygen benzodifuranone (BDF) polymers, which hold significant potential for diverse optoelectronic applications. By employing a simple synthetic route, we have modified side chain lengths. We also systematically explored the structural diversity and its influence on the thermal, optical, and morphological characteristics of BDF polymers.



A simple synthetic route to modify side chain lengths offers versatile means to fine-tune the solubility, film-forming ability, and intermolecular interactions in the polymer matrix. We assess the implications of these structural modifications on the performance of BDF polymers in organic thermoelectrics Our findings underscore the importance of side chain engineering in tailoring the properties of BDF-based materials, paving the way for the development of high-performance optoelectronic devices with enhanced functionality and efficiency.

Shubhradip Guchait (ESR12, Institute Charles Sadron-CNRS, France):

Alignment of conjugated polymers such as regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) is an effective means to enhance charge transport and thermoelectric properties of thin films doped with F_4TCNQ.
In this contribution, we investigate the impact of P3HT regioregularity (RR) on the alignment achieved in thin films by high temperature rubbing and the resulting thermoelectric properties in sequentially doped and aligned films. Structure and thermoelectric properties in doped P3HT thin films are investigated by a combination of transmission electron microscopy (electron diffraction), polarized UV-vis-NIR spectroscopy and thermoelectric measurements (DOI: 10.1021/acsapm.3c00972).



Regioregularity effect on charge conductivity

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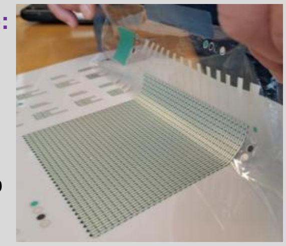
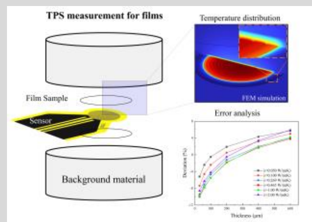
Irene Brunetti (ESR13, InnovationLab GmbH, Germany):
I developed reliable p-type screen-printed vertical TEGs, utilizing silver and free-additive graphene legs. Collaboratively with Federico Ferrari, we've conducted simulations to analyse the behaviour of the TEGs. The devices were scaled up to 10 cm × 10 cm with 800 thermocouples. Now I am manufacturing devices with the same structure, utilizing inorganic materials to power an electronic interface developed by Matías Nicolás Joglar and to use these new TEGs in a real application.

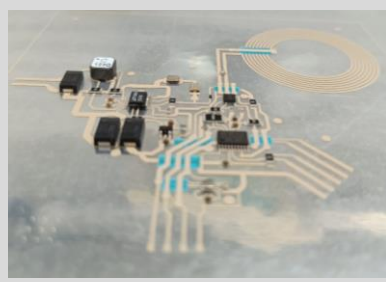


Zijin Zeng (ESR14, HotDisk, Sweden):
Within the project, my focus involves developing novel methods for characterizing thermal transport properties in organic materials. To date, we have introduced and validated a measurement procedure utilizing the Transient Plane Source (TPS) method to determine the cross-plane thermal conductivity of organic films. The proposed procedure is poised to accurately assess the cross-plane thermal conductivity of polymer films ranging in thickness from 50 µm to 600 µm. Additionally, we have developed a finite-element simulation model to enhance our comprehension of heat transfer mechanisms during TPS measurements, with the aim of expanding the capabilities of this method in quantifying thermal transport properties.



TPS method to measure cross-plane thermal conductivity

Matías Joglar (ESR15, Fundació Eurecat, Spain):
So far, I developed DC-DC converters to amplify the voltage of low-power sources, such as thermoelectric generators (TEGs), with alternatives for sources with low or high internal electrical resistance. The latest one aims to the segment of low or medium resistance (around tens of Ohms), to work with TEGs provided by Irene Brunetti (ESR13), and boasts a startup voltage of 22.1 mV and a startup power of around 15 µW, with a minimum conversion ratio $\left(\frac{V_o}{V_i}\right)$ of about 40 times. Furthermore, using a commercial boost converter as its core, I developed an energy harvester over a flexible substrate, to power a microcontroller that can read (and communicate through NFC) the data of an atmospheric sensor.



DC-DC converter

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