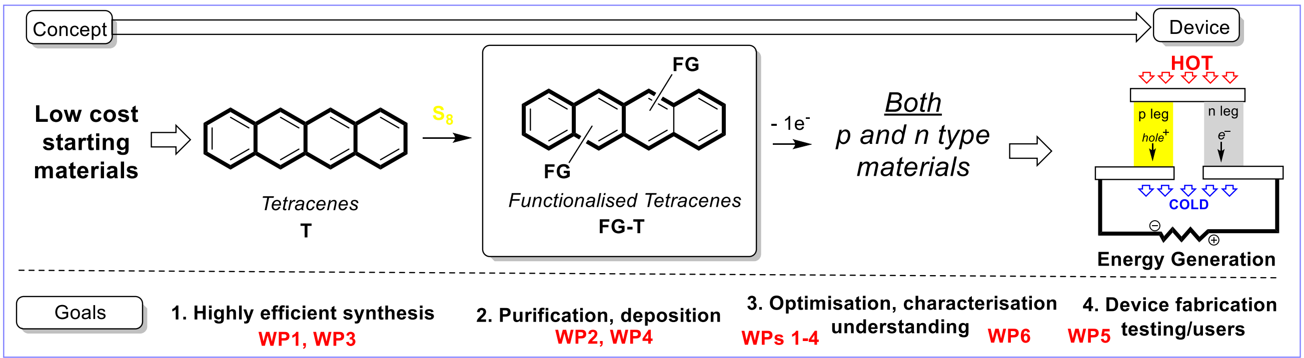
H2ESOT (Project ID 308768)

FP7-ENERGY-2012-1
ENERGY.10.2: FUTURE EMERGING TECHNOLOGIES (FET)
Project full name: Waste Heat to Electrical Energy *via* Sustainable Organic Thermoelectric Devices
Project acronym: H2ESOT
Type of funding scheme: Collaborative Project

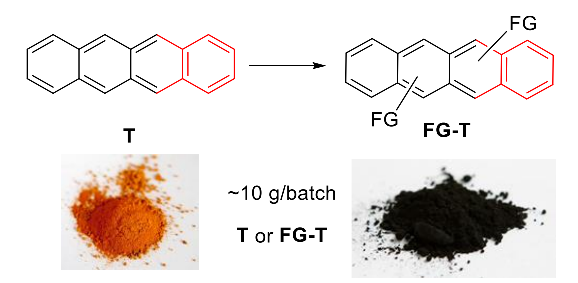
Mid-term - External Summary, month 18
'h2esot' at 10.08.2014

Executive Summary: Anyone who has used a digital thermometer has used the Thermoelectric Effect (TE) for power generation. Basically, any two electrically conducting materials, provided that in one the charge carried by electrons and the other by positive 'holes', when joined generate an electrical current and voltage when heated. The problem is the power generated in a thermocouple is miniscule. For effective Thermoelectric Energy Generation (TEG) from waste heat (we define this as sources below 200 oC) truly exceptional TE materials are needed. In h2esot we are using organic materials based on tetracene. The success of the h2esot project requires completion of the Goals show graphically below:



Progress against these tragets summarised below in Sections 1-4. At the 18 month point the project's progress is in line with its Description of Work (DoW) and its Workpackages (**WP1-6**). We aim deliver one or more TE device types by the end of the programme (month 36), but at this mid-point there are still many issues to be overcome.

Goal 1: Efficient Synthesis. The aim of Workpackages **WP1** and **WP3** were to deliver, either by classical or new chemistry, routes that would provide large (*ca*. 10 g per batch) amounts of **tetracene derivatives** to the programme. This has been achieved through **WP3**, providing the materials shown in Scheme 1. functionalised tetracenes can be modified into both p and n type TE materials: the p type **$(TTT)_2I_3$** is already being prepared in **WP2**. Preliminary investigations in **WP1** indicate an n type material can also be synthesised and that it has appropriate electronic properties (collaboration with **WP4**) and the ability to the form single crystals needed for our project. The major goals of **WP1** and **WP3** are now the achievement of second generation derivatives of tetracenes with improved electronic and physical properties and very efficient routes (high yield, minimum number of steps, sustainable, low cost) to these materials. Screening of successful materials will be through collaboration with **WP4** due to the potential to determine the electronic properties of many samples quickly.



Scheme 1.

Goal 2: Purification and Deposition. Within **WP2** methods for the production of single crystals of **FG-T** and p type materils have been developed; the former are *ca*. 0.8 mm long, while the latter p type are several mm long (Figure 1) The electrical conductivity of the **FG-T** is very low at 298 K. Upon doping under the right conditions this rises to

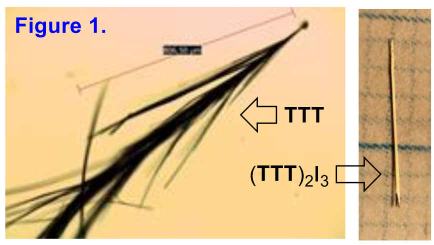


Figure 1.

about the conductivity of graphite. Current optimisation is underway to define conditions that reproducibly deliver p type material of 10-15x higher conductivity (as has been reported before) by manipulation of the crystal's defects and carrier populations. The Seebeck parameters of our p type material are already satisfactory. Presently, single crystal approaches seem to be preferred over deposition of thin films (**WP4**). For example, deposited films of p type material (**TTT**)$_2$I$_3$ show only low electrical conductivity due their polycrystalline nature. However, the ability of the new equipment of **WP4** (Figure 2) to rapidly test small amounts (*ca*. 20 mg per run) allows us to be the first consortium to be able to rapidly screen new 'small molecule' TE materials, *e.g.* confirmation of our n type material was attained this way and our discovery activities are expanding in this area rapidly (collaboration with **WP1** and **WP3**). Single crystal studies of the n type materials are due to begin soon (**WP2**).

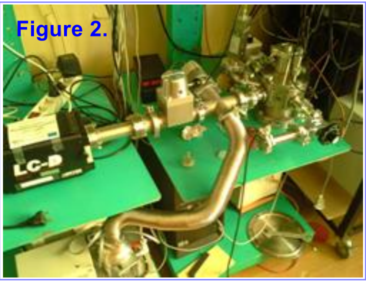


Figure 2.

Goal 3: Optimisation, Characterisation and Understanding. This is a current major focus of the h2esot project to attain superlative p and n type materials it is necessary to control the properties of the crystals to an exquisite level of perfection. While this has been attained occasionally (and often non reproducibly) in previous literature studies of **TTT** materials we are working on defining reproducible conditions for the formations of the best behaving materials. This behaviour has been foreshadowed by computational work in our own consortium (**WP6**) where the crystalline electrical conductivity is a clear function of defect parameter, D_0. As this falls (Figure 3) electrical conductivities are predicted to increase by more than 10-fold leading to an improvement of the performance indicator ZT from 0.1 (poor) to perhaps >2 (indicating an exceptional material). Within the next 18 months we aim to provide experimental data following this theoretical prediction.

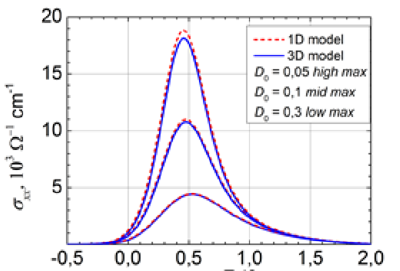


Figure 3.

Goal 4: Device Fabrication and Testing. Fortunately, due to **WP2** being ahead of schedule preliminary fabrication of the elements required to make and test the first of our proto-devices are already underway. Within **WP5** the preparation of mountings for p type (and ultimately n type as well) crystals has already been achieved and an initial test rig is already under construction (Figure 4). While there are many technological obstacles to be overcome, e.g. addressing issues of rapid device fabrication etc. we are pleased that this aspect of the project is also ahead of Schedule.

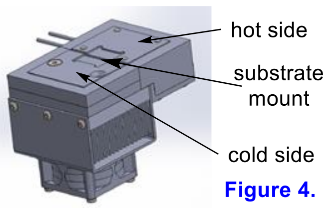


Figure 4.

Impact. Outside the internal reporting of h2esot, the consortium has additionally published 2, directly h2esot related publications and made contributions to 2 others:

1. A .I. Casian, I. I. Sanduleac, Organic thermoelectric materials: new opportunities, *J. of Thermoelectricity* **2013**, 11- 20 [Direct output of project].
2. A. I. Casian, I. I. Sanduleac, Thermoelectric properties of tetrathiotetracene iodide crystals: modeling and experiment, *J. of Electronic Materials* **2014**, *in press* DOI: 10.1007/s11664-014-3105-6 (IF 1.635). [Direct output of project]
3. P. J. Taroni, I. Hoces, N. Stingelin, M. Heeney, E. Bilotti, Thermoelectric Materials: A Brief Historical Survey from Metal Junctions and Inorganic Semiconductors to Organic Polymers, *Isrl. J. Chem.* **2014**, *54*, 534-552. [Supporting publication]
4. I. Sanduleac, A. Casian, J. Pflaum, Thermoelectric properties of tetrathiotetracene iodide crystals in a two-dimensional model, *J. of Nanoelectronics and Optoelectronics* **2014**, *9*, 247-252 (IF 1.038). [Supporting publication].

Additionally, the h2esot programme has become involved in an EU wide TE network and a related national network in the UK. All of the h2esot dissemination activities are documented on the project website (www.h2esot.com) and on the EU participants portal. We aim to release a short video, as the latest addition, in the next two months.