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Chiral oligothiophenes with outstanding chiroptical properties: a powerful innovation in organic optoelectronics performed with the help of *Reaxys®*

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Organic optoelectronics is one of the most promising markets in materials science, thanks to the development of semiconductors based on π-conjugated systems easily processable, highly efficient and compatible with downscaling.[1] Many optical and electrical properties of these compounds (response to external stimuli, light absorption and emission, charge and exciton mobility, etc.) are strongly dependent on their solid-state supramolecular organization.[2] Therefore, the control of nanoscale arrangement by tuning self-assembly processes in thin films is a fundamental strategy to optimize material performance.

Recently, chirality has gained large interest in the fields of metamaterials and organic optoelectronics, as parameter for controlling the supramolecular arrangement of π-conjugated systems at different hierarchy levels: stereodefined elements on their chemical structure can dictate overall chiral architectures, including self-assembled helices, spirals and chiral sheets.[3] These nanostructures also opened the way to a variety of highly innovative technological applications: production or detection of circularly polarized (CP) light, chiroptical switching in information technology, chiral recognition for analytical sensing, electron spin filtering.[4]

Aimed to the possibility of combining the optoelectronic properties of π-conjugated systems with the advantages of chirality, the main project of my PhD work was focused on the synthesis of new chiral π-conjugated oligomers with remarkable chiroptical properties as thin films, in absorption (electronic circular dichroism, ECD) or emission (circularly polarized luminescence, CPL), for potential application in organic optoelectronics. Despite many electronic scientific databases are currently available, Reaxys® has proved to be the most reliable in helping this work, from planning to development.

Due to the lack of reviews on the chiroptical properties of organic π-conjugated systems as thin films, I started providing a comprehensive, authoritative and critical overview of the existing literature on this topic. At this stage, the role of *Reaxys®* was fundamental: using proper keywords in "*Search Reaxys*" field for quick search (**Figure 1**), and then applying some filters to refine the research, I was able to organize this huge literature (more than 400 documents) as function of molecular size and chemical nature of the π-conjugated system.

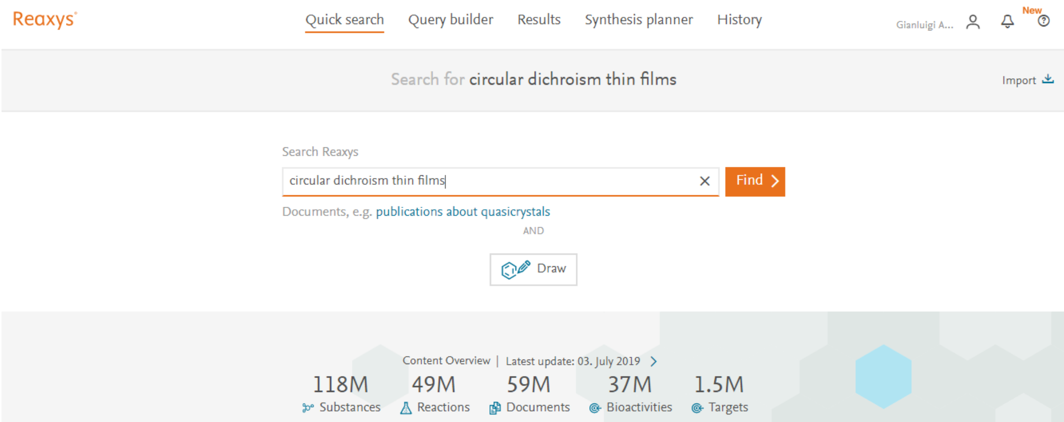

Figure 1. *Chiroptical properties in thin films: document search performed with the help of "Search Reaxys" field.*

From a carefully reading of these papers, oligo/polythiophene-based compounds were considered as the most promising materials for my purposes. Therefore, I worked with π-conjugated systems consisting of a (hetero)aromatic central ring having different stereoelectronic properties, decorated with enantiopure alkyl branched chains and connected to two oligothienyl or oligothienylethynyl units (**Figure 2**).

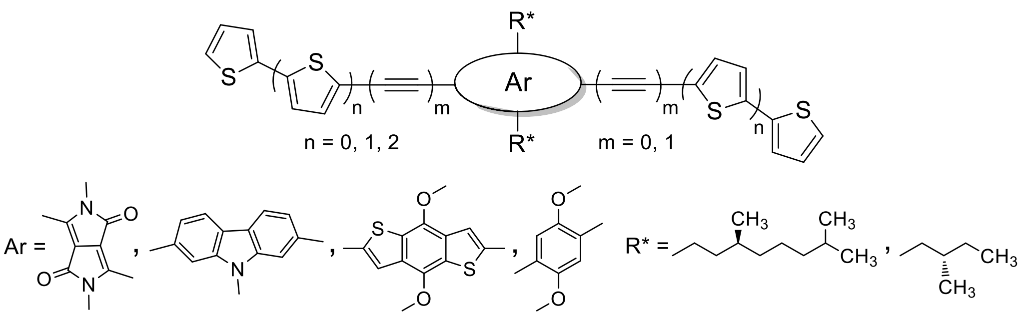

Figure 2. *Chemical structure of chiral oligothiophenes investigated during my PhD research work.*

Interestingly, the *"Draw"* tool of *Reaxys*® for chemical structure-based queries helped me in developing the synthetic strategy of these oligothiophenes: although searching by exact structure the query gave no results (thus demonstrating that designed oligomers are all new compounds), looking for substructures and similarities (**Figure 3**) it was possible to obtain information on the preparation of similar compounds and check commercial availabilities of starting materials (with direct links to producers' websites).

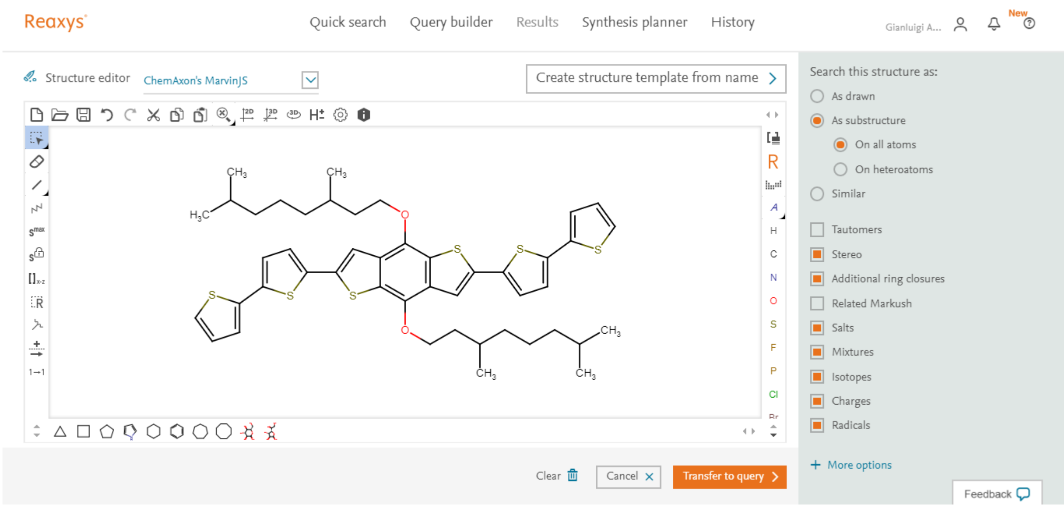

Figure 3. *Search for the designed oligothiophenes through Reaxys® chemical structure-based queries.*

The general synthetic strategy, developed by analysing the results obtained with *Reaxys®*, consisted of three main steps: i) formation of central core, if not commercially available; ii) connection of chiral groups by nucleophilic substitution with alkyl bromides and halogenation of (hetero)aromatic moiety; iii) coupling of two oligothienyl(ethynyl) units through Pd-catalyzed cross-coupling protocols.

I started the chiroptical investigation studying the ECD properties of final oligothiophenes as thin films prepared by drop-casting and spin-coating. Although these samples gave rise to a manifold of situations, some of them exhibited surprisingly and unexpectedly an almost complete ECD signal inversion upon sample flipping (**Figure 4**). Since no examples of this phenomenon were found in my previous literature overview, I used *Reaxys®* for a new document search: in this way, I discovered that it is due to a peculiar interaction between linear dichroism and linear birefringence (named *LDLB effect*), which is only theoretically well understood, while there are no experimental reports to date. This property is absolutely outstanding: opposite chiroptical properties can be obtained with only one enantiomer of a chiral material, simply by considering the two different faces of the same film. In light of the innovation of LDLB effect, which could be exploited for the fabrication of optoelectronic devices able to discriminate the direction of sample illumination, this part of my PhD work was recently published in two papers on *Materials Chemistry Frontiers*[5] and *ChemNanoMat*.[6]

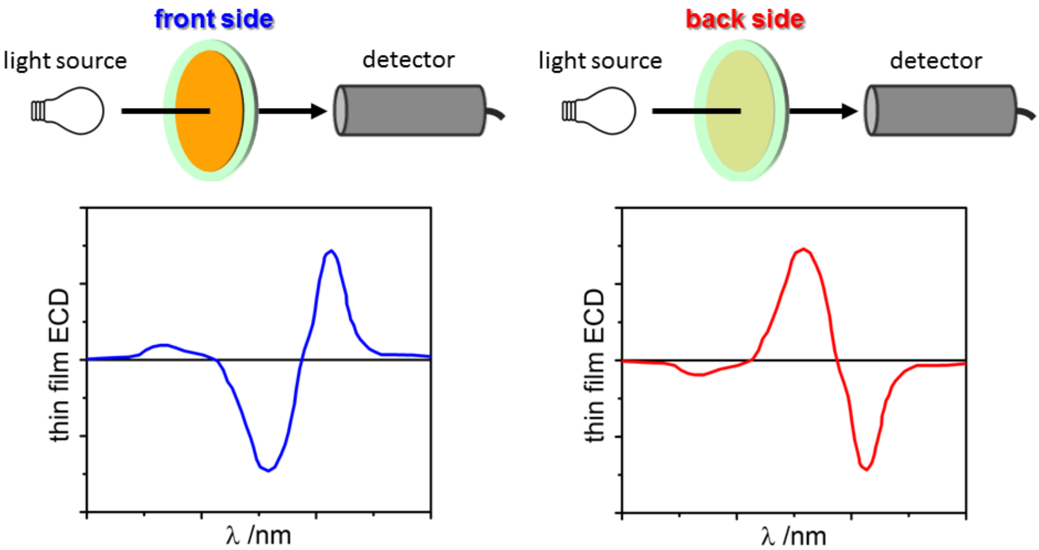

Figure 4. *Schematic representation of the "LDLB effect" observed in some thin films of chiral oligothiophenes.*

The chiroptical properties in emission of chiral oligothiophenes were then investigated: although only part of them showed photoluminescence in thin films, in general CPL spectra with intense signals on a wide wavelengths range were obtained, despite their structural differences. Encouraged by these promising results, in the final part of my PhD work I studied a possible application for this compounds as active layers in CP-light emitting devices (circularly-polarized organic light-emitting diodes, CP-OLEDs), performed during a visiting period at *London Centre for Nanotechnology* of *University College of London (UCL)*.

The development of CP-OLEDs is complicated, due to the reflection of emitted light on the back electrode which reverses the handedness of its circular polarization, resulting in a decrease of circularly polarized electroluminescence (CPEL) signals. Once again, *Reaxys®* was crucial in helping my work: first, through a document search I found papers which addressed this issue by reducing cathode thickness and introducing an additional electron-injecting layer; second, with a new search by substance properties I understood that 2,2',2"-(benzene-1,3,5-triyl)tris[1-phenyl-1*H*-benzimidazole] (TPBi) was the best candidate as electron-injecting material for my purposes (**Figure 5**).

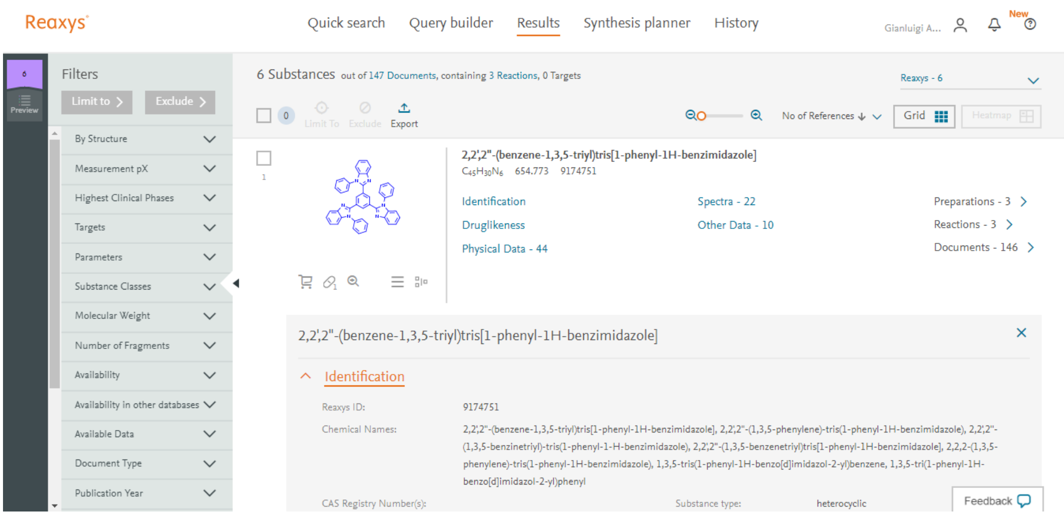

Figure 5. *Reaxys® substance search for the best electron-injecting material for my CP-OLED devices.*

Using the valuable information obtained with *Reaxys®*, I fabricated a *multilayer* CP-OLED based on a 9*H*-carbazole-based oligothiophene as organic semiconductor (**Figure 6**): to the best of our knowledge, it represents the first example of CP-OLED devices based on chiral oligothiophenes as active layers, a *proof-of-concept* device with wide room for improvement, from the chemical structure of the π-conjugated oligomer to the device architecture. Since I am convinced about the novelty and originality of the present work, a paper describing these results is under preparation and it will be published as soon as possible.

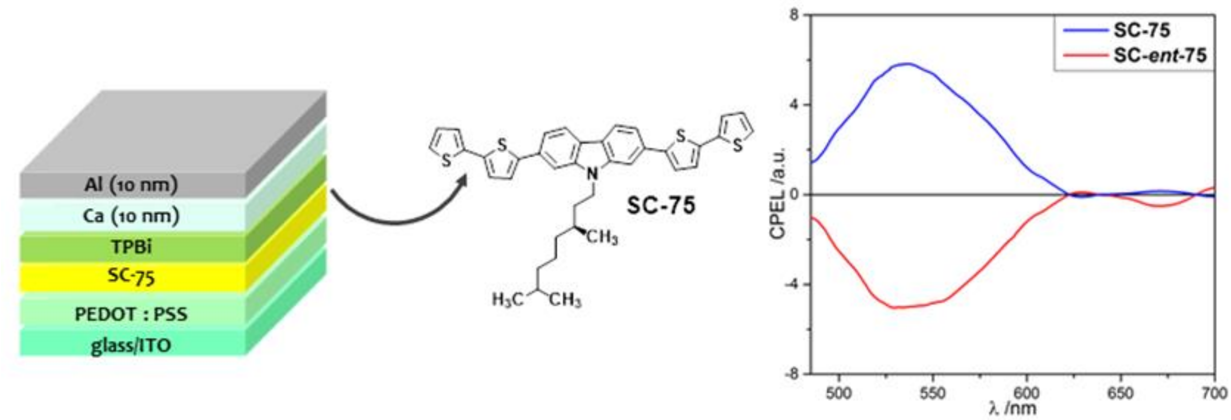

Figure 6. *Schematic representation of the multilayer CP-OLED device based on a 9H-carbazole-based oligothiophene.*

The study performed in my PhD work represents a powerful innovation in the field of organic optoelectronics, describing outstanding chiroptical properties never reported before in literature (*i.e.* the *LDLB effect*) and the development of new optoelectronic devices (*i.e.* the first example of CP-OLEDs based on chiral oligothiophenes). As described above, the role of *Reaxys®* was essential in several steps of this research project, helping me to achieve these important results. In conclusion, I definitely recommend the use of *Reaxys®*: it really allows you to achieve all your goals!

References

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