



‘It just takes the right reaction’

Marco Carlotti

If there is one common element that brings together all the chemistry students of the world, that is to have had at least one professor – usually the organic chemistry professor – which tells you how, back in their days, they needed to memorize all the reactions by heart and do literature search by hand in the department library. Some might even go in all the way by telling that chemists were more prepared in those days and that we young researchers are getting ‘lazy’ in our ways to explore science.

While it is beyond any doubt that chemists in any period of history were able to produce remarkable science regardless the means they had to get the information they needed, we are currently living in an era in which scientific output (and chemistry is not an exception) is growing exponentially to the point that is unimaginable to know everything there is to know about a single discipline. Let alone if you aim to broaden your field of expertise.

During my formation, I changed fields quite often as I wanted to get as much transversal training as possible: I started out studying Inorganic Chemistry, then I graduated with a thesis in polymer chemistry and solid-state NMR, and finally I approached molecular electronics during my PhD. There I had to design and synthesize molecules that could form a self-assembled monolayer (SAM) on metal surfaces and measure their structural and electric properties via various techniques, with the aim of realizing electronic devices in which the active component is only one molecule thick.^[1] We call this a molecular junction.

To be able to investigate these devices, next to learn the fundamentals of quantum mechanics processes that appears at that scale, I needed to develop my skills as an organic synthetic chemist. While it is possible to learn techniques and practical matters from more experienced colleagues, the design of new molecules and synthetic routes is something that requires a lot of study and understanding of the field. For this scope, Reaxys was an indispensable tool, which allowed me to find synthetic procedures for the molecules I designed and provided me with insights for new possible structures.

Among the various issues I tackled in my PhD, this is best exemplified in a project I did about anthraquinoid structures in relation to quantum interference (QI) in molecular tunneling junctions.^[2] QI is a phenomenon related to moving particles whose wave-function can interfere with itself: usually, two electrons cannot interfere with each other since they cannot be defined by the same wave function (i.e. they cannot be in

the same place at the same time), yet, the wave associated with a moving electron can create diffraction patterns if scattered. In tunneling junctions, molecules may act as scattering centers and generate diffraction effects. Destructive QI can lower the conductance of the junction by several orders of magnitude by

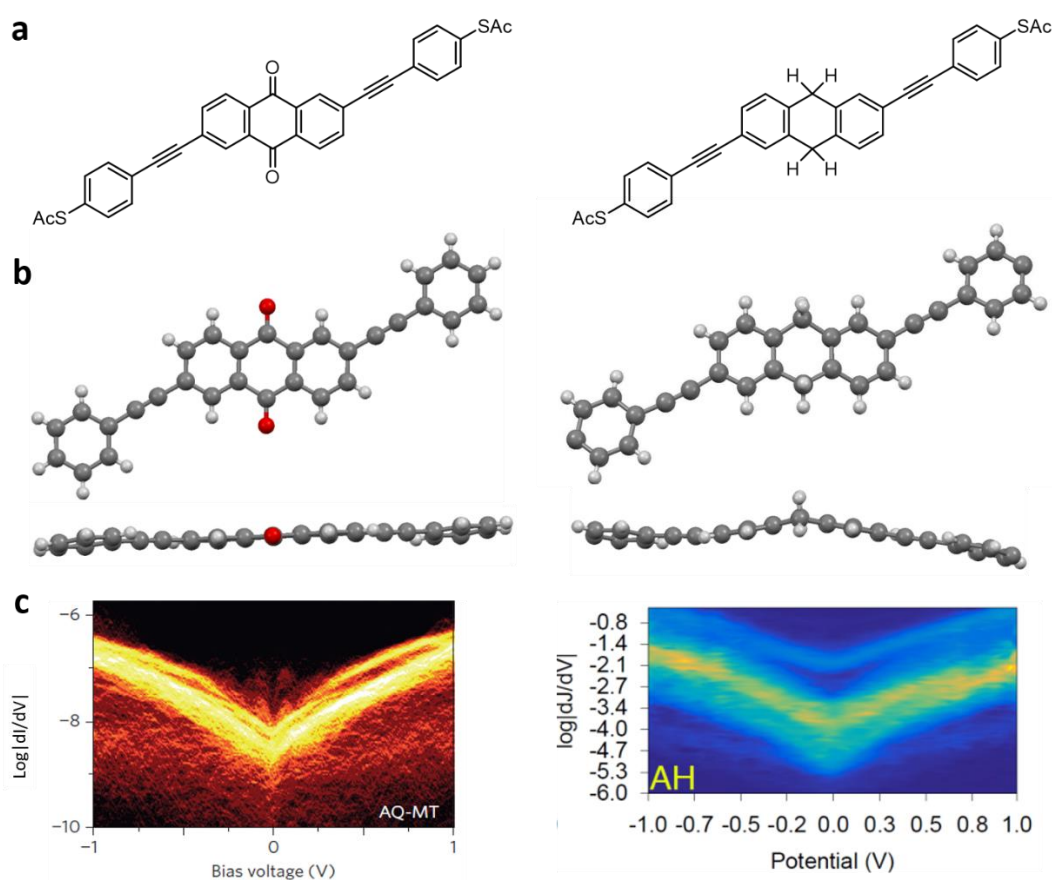


Figure 1. Comparison of anthraquinone (left) and 9,10-dihydro-anthracene (right) molecular wires. *a*: molecular structure; *b*: top and side view of crystal structures; *c*: differential conductance plots of molecular junctions (from [6] and [7]): the V-shape is consistent with the presence of destructive QI.

decreasing the tunneling probability: being able to turn it on and off on command can thus pave the way for responsive molecular electronic devices,^[3] insulating nano-layers^[4] and molecular memories.^[5]

Destructive QI is usually associated with cross-conjugated molecules and meta-substitution in benzene rings. The most iconic and the most used example of this are molecular wires comprising a cross-conjugated anthraquinone core. It was in such system that experimental evidence for QI in molecular junctions was found for the first time (Figure 1).^[6]

At the beginning of my doctoral research I also found evidence for QI while measuring the tunneling properties of a non-cross conjugated molecular wire bearing the 9,10-dihydroanthracene unit:^[7] compared to anthraquinone, the former has similar geometry and dimensions but it is not conjugated because of the sp³-carbon atoms in the 9 and 10 positions. The aromatic rings are anyway held close enough in space that the orbitals can interact edge-to-edge: thanks to this interaction, destructive QI is predicted for this molecule even if the system itself is not fully conjugated. This was the first proof that destructive QI could modu-

late the conductance even in non-conjugated systems and showed that QI has a broader practical range than thought before.

This observation also raised a lot of questions: since both anthraquinone and 9,10-dihydroanthracene are flat, how much of the destructive QI effect in the former is due to the cross-conjugation and how much to the flatness of the core? Would QI still be present in the case of highly bent anthraquinoid structures in which the aromaticity is compromised? What is the role of the carbonyl: does its pronounced electronegativity affect the charge transport at all or is it just a convenient cross conjugated system?

To address these issues, I designed a series of molecular wires which shared the same skeleton as anthraquinone but had different functionalities in place of the carbonyl (Figure 2). In this way, it was possible to address and compare the effects of different substituents in terms of electronic properties, local dipole moments, and steric hinderance that induces bending in the anthraquinoid core. With the help of Reaxys I was able to find the procedures to prepare these compounds taking inspiration from similar substrates.

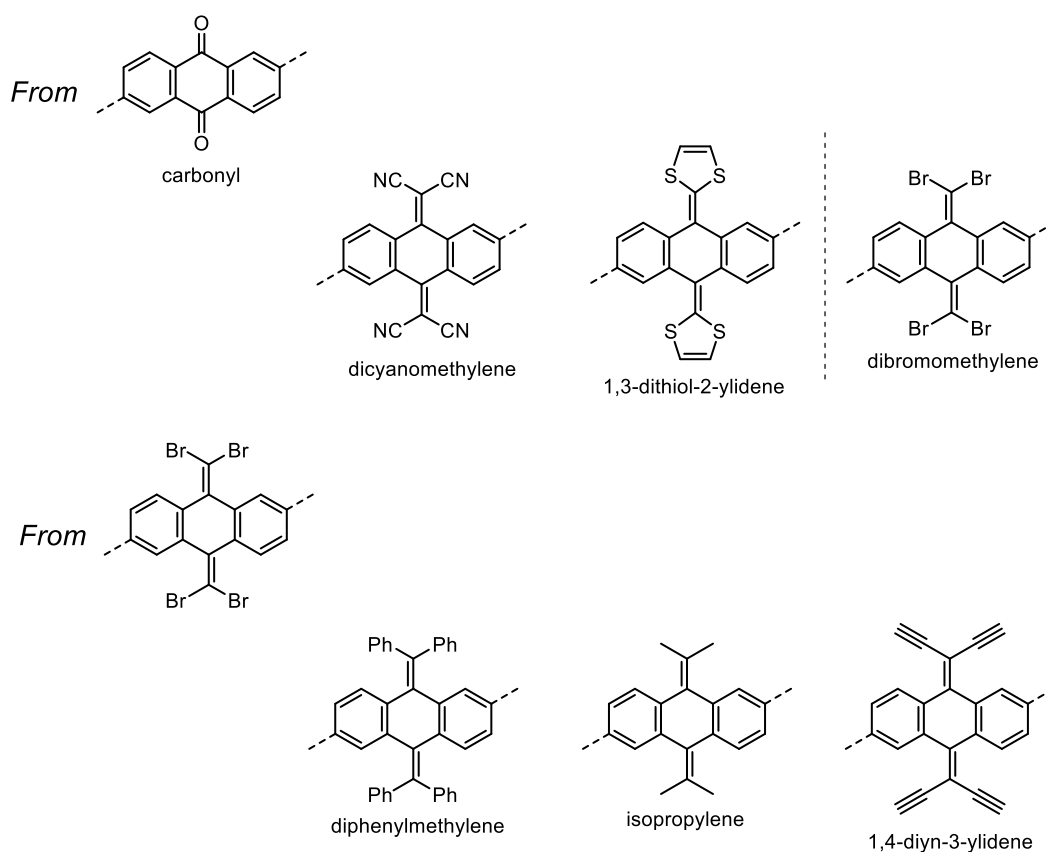


Figure 2. Different anthraquinoid structures prepared in the study.

Unfortunately, I soon came across many difficulties in the synthesis: classic organic carbonyl reactions, such as Wittig or treatment with carbene species, are ineffective in the case of anthraquinone, similarly nucleophilic attacks (followed by elimination) were either ineffective or easily reversed to the starting materials;^[2] starting from substrates different from anthraquinone required too many steps. After months of trial and error I could only synthesize the dicyanomethylene and the 1,3-dithiol-2-ylidene derivatives. While they are

interesting compounds for the project – in particular, the former has a lower LUMO than anthraquinone, the latter a higher HOMO –, with these compounds only, one cannot draw strong conclusions about electronic and geometrical effects.

While trying to figure out new procedures and pathways that would allow me to circumnavigate the synthetic issues on the Reaxys synthetic database, I stumbled across the possibility of adding dibromomethylene groups as in a Corey-Fuchs reaction, an option that I had not considered before (Figure 3). This was an extremely helpful finding as, beside expanding the scope of the series with a new compound, the presence of a bromo-olefin opens a plethora of new synthetic possibilities: by taking advantage of palladium catalyzed coupling reactions I was able to replace the bromine with methyl groups, phenyl rings, and triple bonds, thus accessing a group of all-carbon derivatives necessary to have enough diverse compounds in the series to perform a proper physical organic chemistry.

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6 Conditions [^] Find Similar [>] Reaction ID: 4941138 ⁺

Conditions	Yield	Referenc
With triphenylphosphine In benzene at 20°C; for 24h; Corey-Fuchs olefination;	99%	Donova [Journal 3112] Full Tex
With triphenylphosphine In benzene at 20°C; for 24h;	96%	Bures, I Gross, I [Europe Full Tex]
With triphenylphosphine In dichloromethane at 20°C;	91%	Hwang, [Journal 11248] ...

Figure 3. Preparation of dibromomethylene derivative of anthraquinone suggested by Reaxys.

We systematically studied the performances of these molecular wires in tunneling junctions on different platforms and with computational methods to fully understand the implications in tunneling transport of their electronic, polar, and geometrical characteristics. Thanks to the series of molecular wires prepared, my research group and I were able to show that the electronic effect of the substituents and the distribution of the frontier orbitals dominate the tunneling transport of a molecular junction:^[2] in this sense, wires containing anthraquinone, usually considered as a benchmark, constitute a peculiar class of compounds

which possess the right electronic characteristics to give rise to strong and measurable QI effects, which is not simply arising from the cross conjugation of the core.

Thanks to the myriad of possibilities in synthetic chemistry, one can move the orbitals' energies and modify their distribution without altering the molecular skeleton: controlling the magnitude of the QI effect in different conditions or even ruling it out, can pave the way for functional devices that one day may find technological applications.^[8] We found an example of this in the dicyanomethylene derivative introduced earlier. Once on a metal surface (as it is in the case of a SAM), this compound can spontaneously and reversibly accept electrons from the substrate: upon reduction the cross conjugated core becomes linearly conjugated, thus turning off the QI and increasing the conductance of the molecules by several orders of magnitude.^[4] This behavior, that can be reversed under bias, allowed us to prepare a one molecule-thick memory device that could be activated in situ without the need of a third electrode or an input other than bias. Similar systems could also find application as memristors.^[5]

We just started to unravel the potential of molecular electronic devices, the ones I discussed so far are just two examples among many. What stands between the fundamental science and the technological applications is just the possibility to design and prepare functional compounds that can reliably be incorporated in electronic devices: along this path – which requires the collaboration between chemists, physicists, and engineers – databases like Reaxys will cover an extremely important role in propelling scientific progress forward.

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