Seven years of glyoxylic Perkin strategy: From short ribbons to Möbius rings

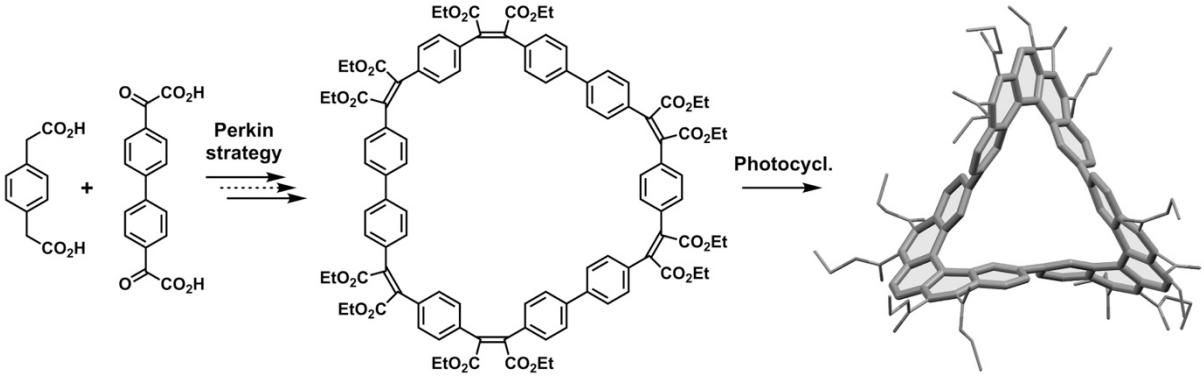
Fabien Durola

CRPP, CNRS & Univ. Bordeaux,115 av. du Dr. Schweitzer
33600 Pessac, France. e-mail: fabien.durola@crpp.cnrs.fr

We have developed an efficient and versatile synthetic approach for the formation of large carboxy-substituted polycyclic arenes. This strategy relies on Perkin reactions for the synthesis of flexible precursors, followed by catalyst- or light-induced cyclization reactions.[1] This synthetic method has been optimized and can now be applied to the formation of non-planar species such as poly-helicenes[2] and large conjugated macrocycles.[3]

The Perkin condensation of bifunctional arylene-diglyoxylic acids with bifunctional arylene-diacetic acids leads to the 2+2 macrocyclic products, where four arylene moieties are connected by four maleic bridges. Depending on the aromatic core and the substitution patterns of the precursors, some of these fully conjugated macrocycles show various atypical geometries, some of them intrinsically chiral.[4]

Finally, the development of complementary protecting techniques for the glyoxylic Perkin reaction have allowed the controlled assembly of a large number of building blocks.[5] Very long phenacenes have been formed, as well as conjugated macrocycles composed of six arylene moieties. One of them has been successfully photocyclized into cyclic tris-[5]helicenes, rigid conjugated macrocycles with single and triple twisted Möbius topologies and Möbius aromaticity.[6]



1 (a) Sarkar, P.; Durola, F.; Bock, H. *Chem. Commun.* **2013**, *49*, 7552; (b) Moreira, T. S.; Ferreira, M.; Dall'armellina, A.; Cristiano, R.; Gallardo, H.; Hillard, E. A.; Bock, H.; Durola, F. *Eur. J. Org. Chem.* **2017**, 4548.

2 (a) Bock, H.; Huet, S.; Dechambenoit, P.; Hillard, E. A.; Durola, F. *Eur. J. Org. Chem*. **2015**, 1033; (b) Ferreira, M.; Naulet, G.; Gallardo, H.; Dechambenoit, P.; Bock, H.; Durola, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 3379.

3 Robert, A.; Dechambenoit, P.; Bock, H.; Durola, F. *Can. J. Chem.* **2017**, *95*, 450.

4 Robert, A.; Dechambenoit, P.; Hillard, E. A.; Bock, H.; Durola, F. *Chem. Commun.* **2017**, *53*, 11540.

5 (a) Naulet, G.; Robert, A.; Dechambenoit, P.; Bock, H.; Durola, F. *Eur. J. Org. Chem.* **2018**, 619; (b) Naulet, G.; Huet-Exiga, S.; Bock, H.; Durola, F. *Org. Chem. Front.* **2019**, *6*, 994.

6 Naulet, G.; Sturm, L.; Robert, A.; Dechambenoit, P.; Röhricht, F.; Herges, R.; Bock, H.; Durola, F. *Chem. Sci.* **2018**, *9*, 8930.