

# Helicenes, Chiral Nanographenes and Polysulfurated Arenes with Dynamic and Outstanding Properties in Novel Aromatic and Materials Chemistry

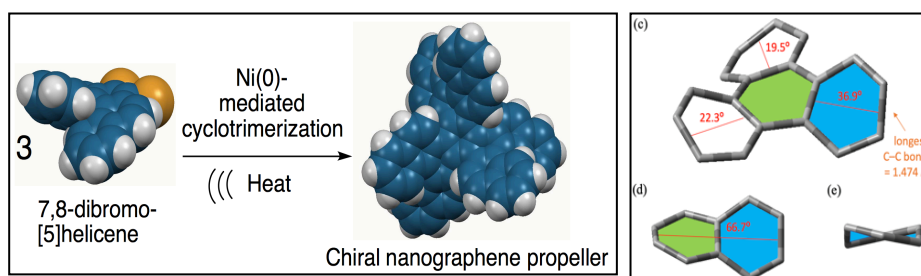
Pr. Marc Gingras

Aix-Marseille Université, CNRS, CINAM, 13009 Marseille, France

e-mail: marc.gingras@univ-amu.fr

## Abstract :

The first part of this lecture comprises helicenes with their chiral distorted  $\pi$ -system, which are known for over 120 years.<sup>1</sup> Their attractiveness is not only due to their syntheses<sup>2</sup> and helicity, but mostly to their exalted chiroptical, electronic and supramolecular properties.<sup>1</sup> They became the center of expanding subfields in asymmetric catalysis, molecular electronics, optics, spintronics and supramolecular assemblies,<sup>1b</sup> either on metal surfaces<sup>2b,3</sup> or on insulators.<sup>4</sup> Lately, triple-fused helicenes embedding six helicene motifs were reported among the first stable chiral nanographenes with a record distortion of a benzene ring, bond length alternation (Kékulé model), local aromaticity and metal ions complexation.<sup>5,6</sup> It contributes to explore aromaticity and the expanding field of stable chiral nanographenes.



A second part will report peculiar perthioarenes and polythiophenylene architectures of various topologies, their synthesis, and a survey of applications in materials science. They comprise asterisks, dendrimers and distorted molecules, which often incorporate dense sulfur and arene units,<sup>7</sup> leading to multifunctional and highly luminescent (phosphorescent and fluorescent)<sup>8</sup> nano-objects and sensors.<sup>9,10</sup> They represent an underexploited class of aromatic systems with rich supramolecular interactions, chiroptical and electronic properties, which could be modulated by some metal interactions, cation- $\pi$  interactions and by some  $\pi$ - $\pi$  complexes. Amongst the utmost important properties, pioneer dynamic covalent aromatic chemistry will be reported from the reversible nature of nucleophilic aromatic substitutions ( $S_NAr$ ), thus enlighting new avenues in aromatic chemistry involving countless  $S_NAr$  reactions. One could call it : "The Sulfur Dance" around arenes and heteroarenes.<sup>11,12</sup>

Overall, this lecture will provide new insights in modern aromatic, dynamic and materials chemistry for the near future.

**References :** 1) (a) M. Gingras, *Chem. Soc. Rev.* **2013**, 42, 968; (b) M. Gingras, *ibid* **2013**, 42, 1051; (c) M. Gingras et al. *ibid* **2013**, 42, 1007. 2) (a) M. Gingras et al. *RSC Adv.* **2014**, 4, 32412; (b) M. Gingras et al. *Org. Lett.* **2009**, 11, 3846. 3) Y. Coquerel, M. Gingras, K.-H. Ernst et al. *Chem. Eur. J.* **2021**, 27, 10251. 4) (a) C. Barth, M. Gingras et al. *Adv. Mater.* **2012**, 24, 3228; (b) M. Gingras, C. R. Henry, C. Barth et al. *J. Phys. Chem. C* **2014**, 118, 14569. 5) Y. Coquerel, M. Gingras et al. *J. Am. Chem. Soc.* **2017**, 139, 18508. 6) M. Gingras, Y. Coquerel et al. *Angew. Chem. Int. Ed.* **2020**, 59, 3264. 7) M. Gingras, J.-M. Raimundo, Y. M. Chabre, *Angew. Chem. Int. Ed.* **2006**, 45, 1686; 8) A. Fermi, G. Bergamini, R. Peresutti, E. Marchi, M. Roy, P. Ceroni, M. Gingras, *Dyes and Pigments* **2014**, 110, 113. 9) A. Fermi, G. Bergamini, M. Roy, M. Gingras, P. Ceroni, *J. Am. Chem. Soc.* **2014**, 136, 6395. Highlighted as one of the 6 publications of the week on May 26, 2014, as "Noteworthy Chemistry" by ACS, <http://www.acs.org/content/acs/en/noteworthy-chemistry/2014-archive/may-26.html#nc3>. 10) M. Villa; B. Del Secco; L. Ravotto; M. Roy; E. Rampazzo; N. Zaccheroni; L. Prodi; M. Gingras; S. Vinogradov; P. Ceroni *J. Phys. Chem. C* **2019**, 123, 49, 29884. 11) S. Gahlot, A. Gradone, M. Roy, M. Giorgi, S. Conti, P. Ceroni, M. Villa, M. Gingras, *Chem. Eur. J.* **2022**, e20220097. 12) "The Sulfur Dance Around Arenes and Heteroarenes - The Reversible Nature of Nucleophilic Aromatic Substitutions" S. Gahlot, J.-L. Schmitt, A. Chevalier, M. Roy, M. Villa, P. Ceroni, J.-M. Lehn, M. Gingras, *Chem. Eur. J.* **2024**, e202400231 <https://doi.org/10.1002/chem.202400231>