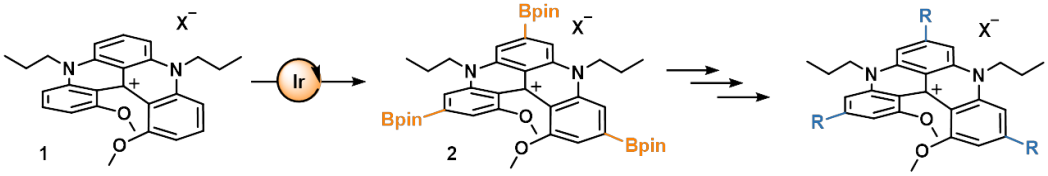
Neutral Radical Chromophores based on Triple-Functionalized [4]Helicene Scaffolds

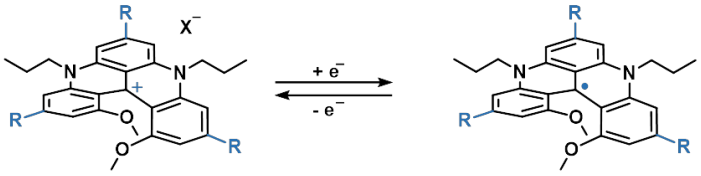
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Helicenes are chiral *ortho*-condensed polyaromatics that, for purely organic derivatives, usually display absorption, fluorescence, electronic circular dichroism (ECD) and circularly polarized luminescence (CPL) in the blue range of the visible spectrum.[1,2] Cationic [n]helicenes are, however, welcome exceptions. In fact, the extended delocalization provided by the triarylcarbenium framework allows the targeting of longer visible wavelengths and even of the NIR spectral region.[3] Late-stage functionalization is then a particularly attractive strategy to manipulate the core helical structures, as it renders the synthesis time-efficient while favouring a large scope of products.[3]



In this work, a new family of poly-functionalized cationic [4]helicenes was prepared. Thanks to Ir-catalyzed direct C-H borylations, a triple *para*-functionalization to the formal positive charge has been achieved on the classical scaffold **1**.[4] Tris-borylated **2** is not isolable *per se*, but each BPin moiety is readily transformed through tandem reactions into various functional groups. These newly introduced substituents, depending on their electron-donating (ED) or electron-withdrawing (EW) nature, strongly influence the electronic and optical properties of the helical core (*e.g.*, redox potentials, energy band gap, Φ_f and lifetime). Interestingly, the derivatives bearing EW groups show an enhanced stability upon mono reduction leading to neutral radical species. These radical helicenes present increased ECD at low energies compared to the parent helical cations with g_{abs} values above 10^{-3} (λ ~ 700-900 nm).



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3. a) Irene Hernández Delgado, Simon Pascal, Antoine Wallabregue, Romain Duwald, Céline Besnard, Laure Guénée, Christoph Nançoz, Eric Vauthey, Roberto C. Tovar, Jamie Lunkley, Gilles Muller, Jérôme Lacour, *Sci.* **2016**, *7*, 4685-4693. b) Johann Bosson, Géraldine Labrador, Céline Besnard, Denis Jacquemin, Jérôme Lacour, *Angew. Chem. Int. Ed.* **2021**, 60, 8733-8738.
4. Lucas Frédéric, Bibiana Fabri, Laure Guénée, Francesco Zinna, Lorenzo Di Bari, Jérôme Lacour, *Eur. J.* **2022**, e202201853.