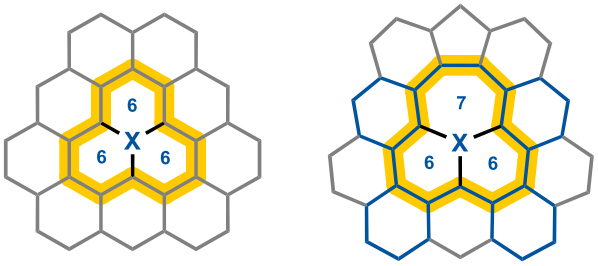
Perfectly imperfect chiral molecules – the access to radicals and boron/phosphorus-doped materials

Krzysztof Dzieszkowski, Paweł Mitka, Miłosz Pawlicki

Functional Organic Materials Research Group
Faculty of Chemistry
Jagiellonian University in Kraków
web: http://mjplab.org
e-mail: krzysztof.dzieszkowski@uj.edu.pl

The modulation of π-extended molecular properties entails the implementation of some "*imperfections*" into the structures of meticulously designed materials. The incorporation of a specific defect to a π-cloud (*e.g.* charge, empty p_z orbital etc.) can cause a significant change in optical properties, including an enhancement of fluorescence quantum yield. The behaviour observed in nanographenes can be easily transferred to relatively small macrocycles modified by the interaction with electron-donating or electron-withdrawing heteroatom. Consequently, macrocyclic molecules with predefined places for boron or phosphorus doping in a *6.6.6* or *7.6.6* fashion are intensively developed as a new branch of organic materials.[1]



The abovementioned post-synthetic modification of obtained molecules *via* incorporation of a heteroatom is also an easy access to switch between completely different redox and optical properties. Furthermore, π-extended molecules can also be "*defected*" by the extraction of one electron generating a usually unstable open-shell system exhibiting entirely different optical, magnetic, and redox properties.[2,3] What is particularly appealing, some macrocyclic molecules can surprisingly stabilize an open-shell unit enabling the synthesis of rather stabile radical materials. Last but not the least, the "*imperfection*" that can be introduced into new materials is the lack of symmetry usually seen by a human eye as something less comely than ideal symmetry. The axial or helical chirality of electronic materials opens several possibilities for new chiroptical properties development, including the emission of circularly polarized light (CPL).[4]

The strategy of the synthesis of novel macrocyclic molecules based on well-known diarylamine moiety will be presented. The extraordinary behaviour of obtained molecules resulted in the development of radical/radical cation systems and boron/phosphorus(III/V) doped materials together with a unique synthetic approach to obtain those derivatives. Moreover, the properties of molecules mentioned so far were examined by molecular spectroscopy (NMR, EPR, UV-Vis, SF, and CD), followed by X-ray crystallography and theoretical support.

References:

[1] K. Dzieszkowski, M. Pawlicki, *Mater. Chem. Front.*, **2022**, *6*, 3306-3317
[2] P. Murto, H. Bronstein, *J. Mater. Chem. C*, **2022**, *10*, 7368-7403
[3] A. Mizuno, R. Matsuoka, T. Mibu, T. Kusamoto, *Chem. Rev.*, **2024**, *124*, 1034-1121
[4] K. Dhbaibi, L. Faverau, J. Crassous, *Chem. Rev.*, **2019**, *119*, 8846-8953