



Nanohoop size influence in bridged cyclo-*para*-phenylenes

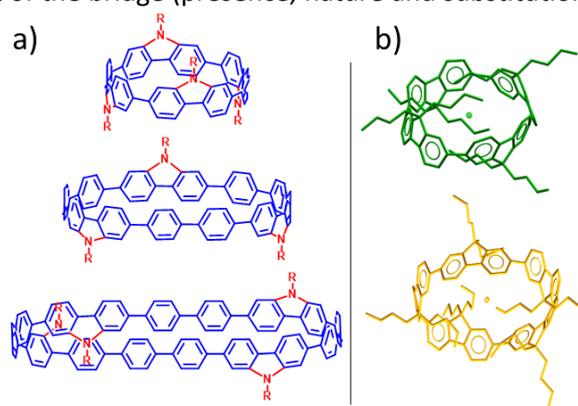
Cassandre Quinton,^a Fabien Lucas,^a Lambert Sicard,^a Joëlle Rault-Berthelot,^a Cyril Poriel^a

^aUniv Rennes, CNRS, ISCR-UMR 6226, 35000 Rennes, France. Email: cassandre.quinton@univ-rennes1.fr

Abstract:

Since 2008 and the synthesis of the first cyclo-*para*-phenylene (CPP),¹ which is the cyclic association of phenyl units *via* para linkages, hoop-shaped π -conjugated macrocycles possessing radially directed π -orbitals (so called "nanohoops") have been subject to intense research worldwide.²⁻⁴ Compared to their linear counterparts, nanohoops possess unique electronic and structural characteristics.⁵ In 2016, Nuckolls and co-workers have shown the several advantages of cyclic oligomers over corresponding linear counterparts in electronics devices.⁶ In 2019, theoretical calculations have predicted the strong potential of CPPs as high mobility materials.⁷ Since then, we showed that cyclo-2,7-carbazoles can be used as an active layer in an organic field-effect transistor (OFET) and provided a first benchmark in term of OFET characteristics for this type of cylindrical π -conjugated systems. We performed a detailed structure-properties-device performance relationship study of three cyclo-2,7-carbazoles bearing different alkyl chains on their nitrogen atoms, cyclo-2,7-fluorene and cyclo-*para*-phenylene in order to shed light on the impact of the bridge (presence, nature and substitution) in bridged cyclo-*para*-phenylenes.^{8,9}

Considering the field of nanohoops, the influence of the hoop size on the electronic properties is probably the most fascinating feature.² However, if this has been deeply studied in the case of CPPs, it is far to be the case for the other nanohoop families. In the present work, we compare the structural, optical and electrochemical properties of several nanohoops displaying different sizes (3, 4 or 5 constituting units) within two families of bridged cyclo-*para*-phenylenes, the cyclo-2,7-carbazoles and the cyclo-2,7-fluorenes,¹⁰ in order to shed light on the evolution of the properties upon size. The findings concerning the evolution of the frontier orbitals upon size could be used to design nanohoop-based semi-conductors with HOMO/LUMO levels fitting a desired application. Regarding the photophysics, the evolution of the absorption properties in solution upon size is specific to bridged cyclo-*para*-phenylenes whereas the evolution of the fluorescence properties follows the rules defined for CPPs. For all nanohoops, defining the evolution of their structural and electronic properties as a function of the hoop size is a crucial step in the understanding of these new generations of π -conjugated systems and their possible applications. This is the aim of this work.



Structures of the studied nanohoops based on
a) carbazole units, b) fluorene units

References: (1) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646. (2) Darzi, E. R.; Jasti, R. *Chem. Soc. Rev.* **2015**, *44*, 6401. (3) Omachi, H.; Segawa, Y.; Itami, K. *Acc. Chem. Res.* **2012**, *45*, 1378. (4) Lewis, S. E. *Chem. Soc. Rev.* **2015**, *44*, 2221. (5) Sicard, L.; Jeannin, O.; Rault-Berthelot, J.; Quinton, C.; Poriel, C. *ChemPlusChem* **2018**, *83*, 874. (6) Ball, M.; Zhong, Y.; Fowler, B.; Zhang, B.; Li, P.; Etkin, G.; Paley, D. W.; Decatur, J.; Dalsania, A. K.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2016**, *138*, 12861. (7) Lin, J. B.; Darzi, E. R.; Jasti, R.; Yavuz, I.; Houk, K. N. *J. Am. Chem. Soc.* **2019**, *141*, 952. (8) Lucas, F.; McIntosh, N.; Jacques, E.; Lebreton, C.; Heinrich, B.; Donnio, B.; Jeannin, O.; Rault-Berthelot, J.; Quinton, C.; Cornil, J.; Poriel, C. *J. Am. Chem. Soc.* **2021**, *143*, 8804. (9) Lucas, F.; Sicard, L.; Jeannin, O.; Rault-Berthelot, J.; Jacques, E.; Quinton, C.; Poriel, C. *Chem. Eur. J.* **2019**, *25*, 7740. (10) Sicard, L.; Lucas, F.; Jeannin, O.; Bouit, P. A.; Rault-Berthelot, J.; Quinton, C.; Poriel, C. *Angew. Chem. Int. Ed.* **2020**, *59*, 11066.