Selected Topic	Topic 1: Fullerenes, Carbon Nanotubes, Graphene, Carbon Dots, and Related Nanostructures

[n]Cycloparaphenylenes with Charges: Cyclic Conjugation at Last

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Oligophenylenes (polyphenylenes) are constituted by an array of π–conjugated benzenes where inter-ring electron delocalization tends to extend over the whole chain (linear π–conjugation) being intrinsically limited, among other factors, by terminal effects. Alternatively, *cyclic conjugation* is envisaged as the unlimited free-boundary version of π–conjugation which will impact the structure of molecules in rather unknown ways. The cyclic version of oligophenylenes, cycloparaphenylenes ([n]CPPs with *n* the number of phenyl rings) were first synthesized in 2008 by Beztozzi and Jasti.[1] Today the whole [n]CPP series from [5]CPP to [18]CPP has been prepared. [n]CPPs represent ideal models to investigate new insights of the electronic structure of molecules and *cyclic π–conjugation* when electrons or charges circulate in a closed circuit without boundaries.

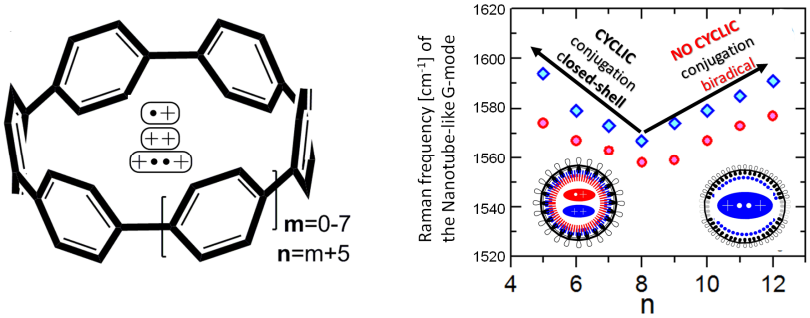

Figure 1. Chemical structures of [n]CPP and **V-shape** behavior of the Raman frequencies.

Radical cations and dications of [n]CPP from *n*=5 to *n*=12 have been prepared and studied by Raman spectroscopy.[2] Small [n]CPP dications own their stability to the closed-shell electronic configuration imposed by *cyclic conjugation*. However, in large [n]CPP dications *cyclic conjugation* is minimal and these divalent species form open-shell biradicals. The Raman spectra reflect the effect of cyclic conjugation in competition with cyclic strain and biradicaloid aromatic stabilization. Cyclic conjugation provokes the existence of a turning point or **V-shape** behavior of the frequencies of the G bands as a function of *n*. In this communication we will show the vibrational spectroscopic fingerprint of this rare form of conjugation.

[1] R. Jasti, J. Bhattacharjee, J. B. Neaton, C. R. Bertozzi, "Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]Cycloparaphenylene: Carbon Nanohoop Structures", *J. Am. Chem. Soc*. *130* (2008), 17646–17647.
[2] M. P. Alvarez, P. M. Burrezo, M. Kertesz, T. Iwamoto, S. Yamago, J. Xia, R. Jasti, J. T. L. Navarrete, M. Taravillo, V. G. Baonza, J. Casado, "Properties of Sizeable [n]CycloParaPhenylenes As Molecular Models of Single-Wall Carbon Nanotubes By Raman Spectroscopy: Structural and Electron-Transfer Responses Under Mechanical Stress", *Angew. Chem. Int. Ed*. *53*, (2014), 7033−7037.