

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

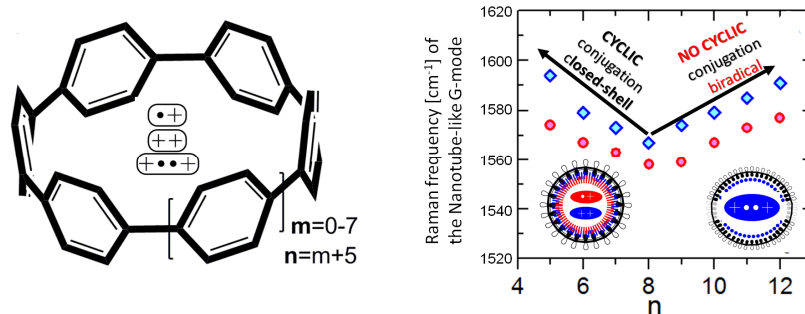


Figure 1. Chemical structures of [n]CPP and **V-shape** behavior of the Raman frequencies.

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 Nano-hoop 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.