On the synthesis of a metal chelating terpyridine-based bilayer nanographene

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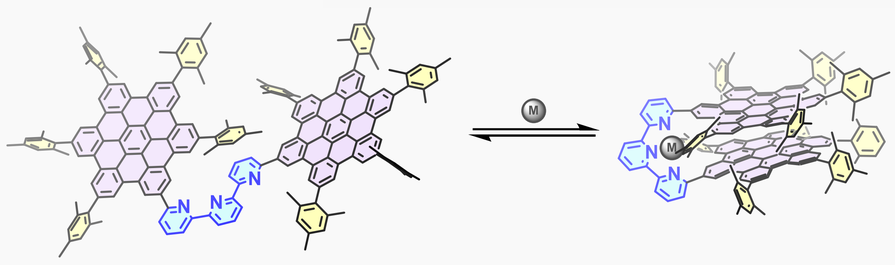
Introduction

Nanographenes are defined as nanometric scale graphene fragments (1-100 nm), and can be synthesized both with bottom-up and top-down methods. Among different bottom-up approaches, organic synthesis provides excellent control over the structure and, therefore, the properties of the molecule. [1]

While pristine graphene is a semimetal, molecular nanographenes's electron confinement confers them a notable HOMO-LUMO gap. This is interesting for applications like semiconductors, photovoltaics and OLEDs.

Objectives

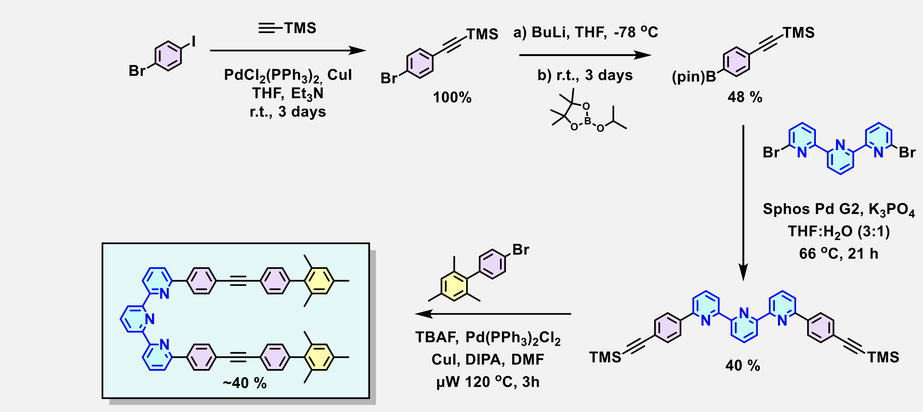


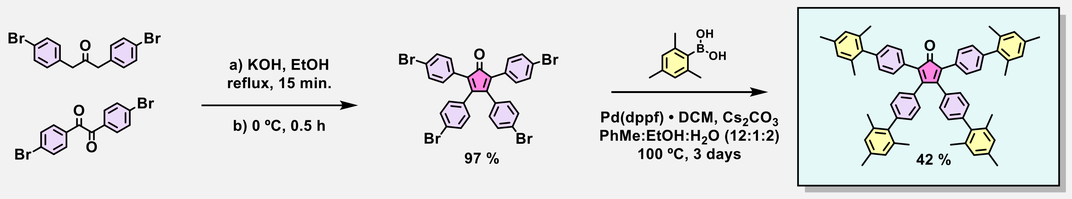
The synthesis of a terpyridine-based bilayer nanographene is proposed. The molecule has been designed by combination of three main components.

- **Nanographene:** Its main goal is to interact with light, either by absorbing it or by emitting it.
- **Terpyridine:** It serves as a molecular switch, opening or closing the molecule depending on if a metal is coordinated to it or not. [2]
- **Mesityl:** It serves as a solubilizing agent, preventing aggregation.

Potential applications of this molecule include spin-transition materials, luminiscent materials and photocatalytic materials.

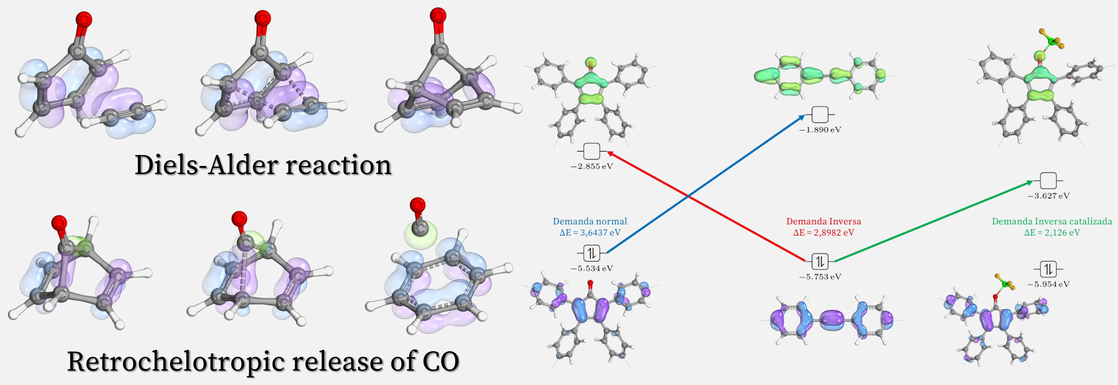
Precursors Synthesis



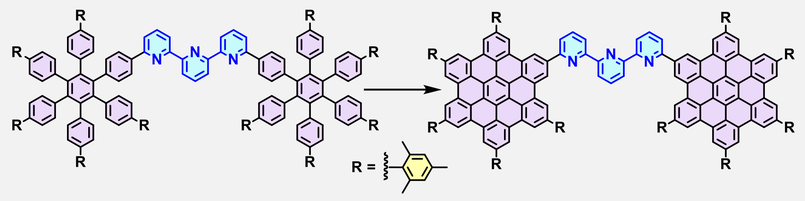


Nanographene Synthesis

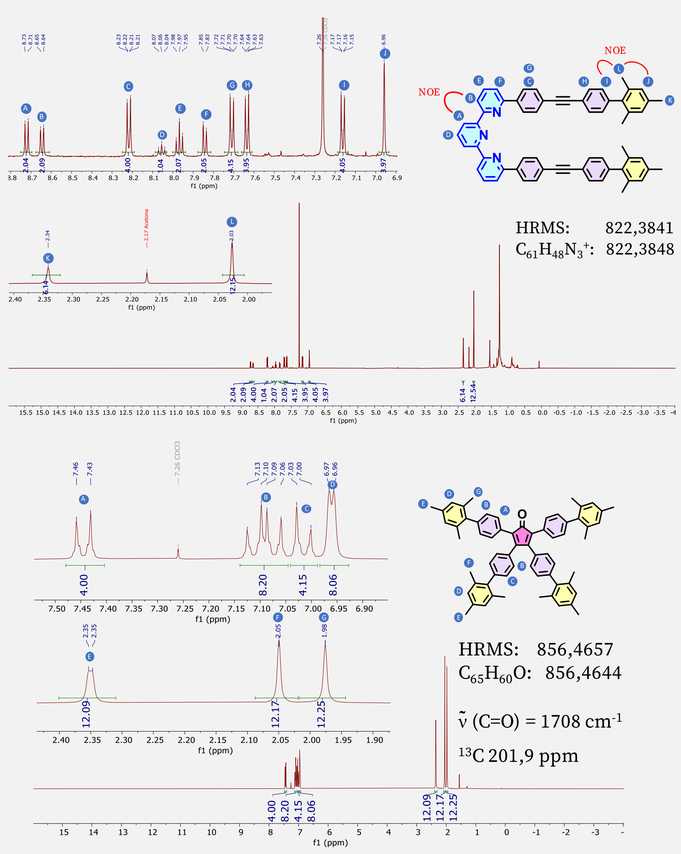
Two subsequent pericyclic reactions between the precursors lead to the formation of the polyarene. Their model reactions have been calculated at the B3LYP-D3/def2-SVP level of theory. Reactive orbitals are represented through the IBO method. [3] Also, the demand of the Diels-Alder reaction has been calculated to belong to the inverse kind.



Finally, a Scholl reaction would be carried out, yielding the graphitized product.

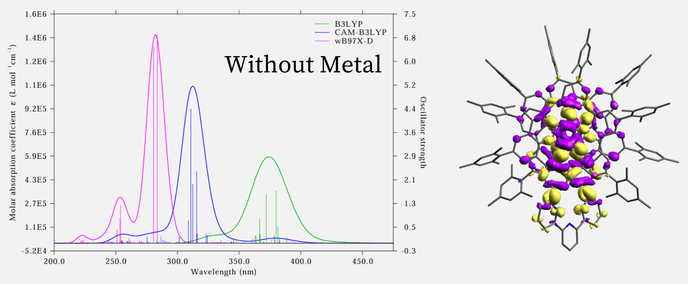


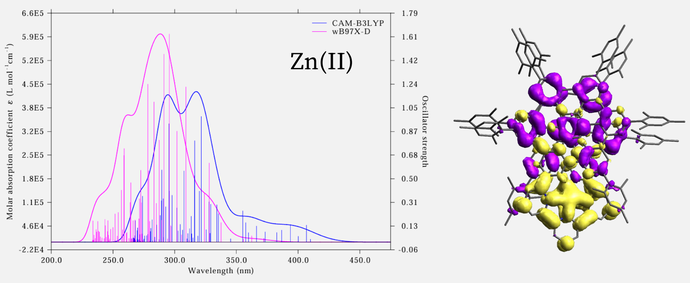
Characterization



UV-VIS Absorption

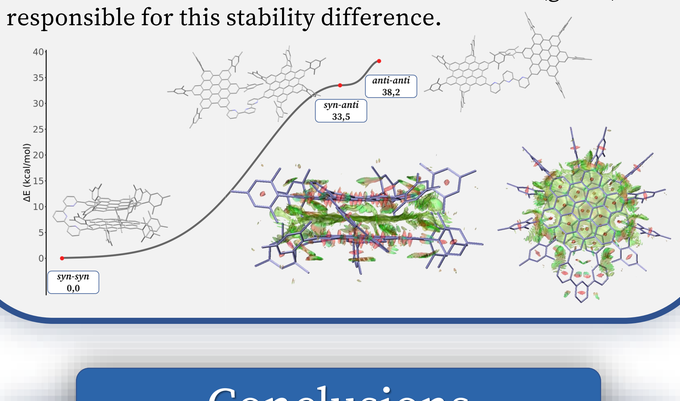
Since the final molecule has not been achieved yet, UV-VIS absorption spectra could not be measured. However, it has been theoretically calculated both for the metal-free molecule, and for the Zn(II) coordinated one. In this last case, the most intense transition corresponds to a charge transfer from the nanographene to the metal.





Conformational Study

The bilayer conformation (*syn-syn*) is about 30 kcal/mol more stable than any open conformation, meaning the molecule will stay closed even when no metal is present. Intramolecular π-π and CH-π interations (green) are responsible for this stability difference.



Conclusions

- The two main precursors of a terpyridine-based bilayer molecular nanographene have been sucessfully synthesized and characterized.
- Due to complications in the reproducibility of the synthesis of the dialkynillic precursor, the final nanographene has not been synthesized yet.
- Computational studies showed that the Diels-Alder reaction belongs to the inverse kind, and that the molecule will stay in its bilayer conformation even in absence of any metal coordination.
- Theoretical absorption UV-VIS spectra showed a charge transfer transition from the nanographene to the metal.

References

[1] Martin, N.; Nuckolls, C. P. Molecular Nanographenes: Synthesis, Properties, and Applications; John Wiley & Sons, 2025.
[2] *Chem. Commun.* **2015**, *51*, 12916–12919.
[3] *Angew. Chem., Int. Ed.* **2015**, *54*, 5518–5522.