



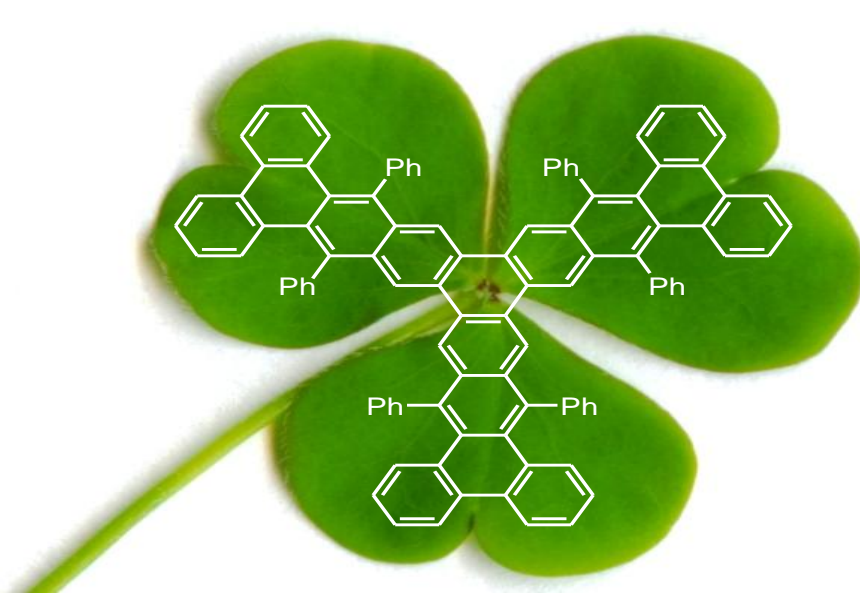
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Cycloaddition reactions involving arynes are extremely useful tools for the convergent synthesis of polycyclic aromatic structures. In particular, the metal catalyzed [2+2+2]-cycloadditions of arynes, first described by our group ten years ago^[1-3], and the tandem variants of the classical Diels-Alder reaction, provide novel and efficient methods for the controlled synthesis of large and/or complex polycyclic aromatic hydrocarbons (PAHs) of interest for the development of novel functional materials, including nanographenes. The following chart shows some of our recent examples of the application of this concept.

Structurally complex PAHs:

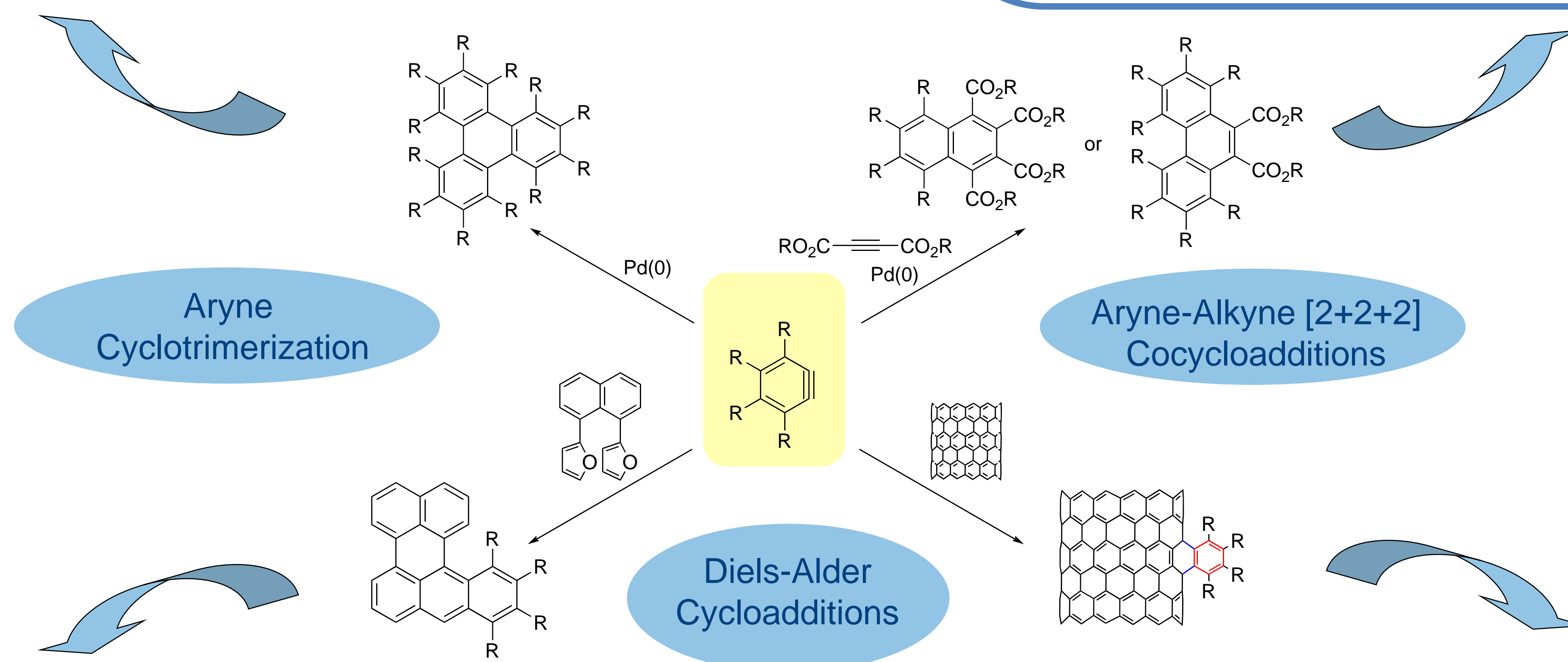
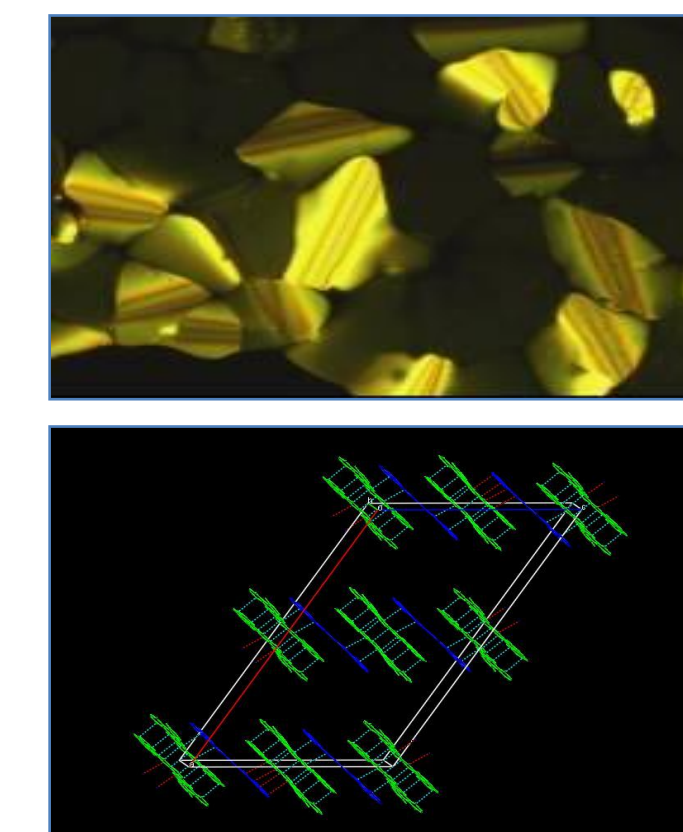
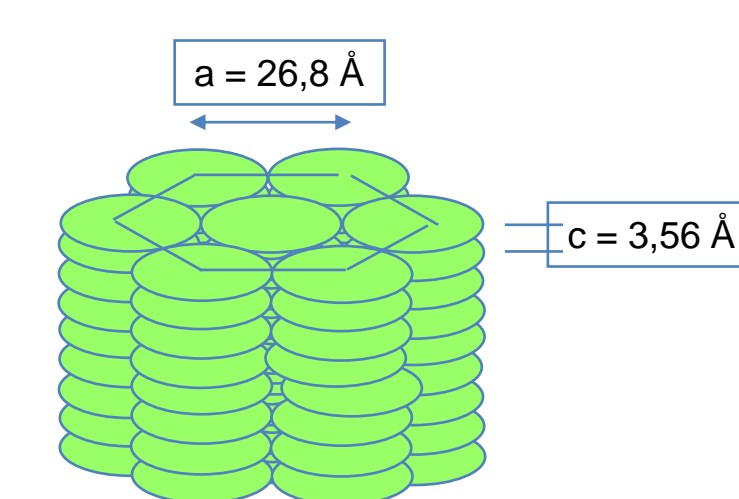
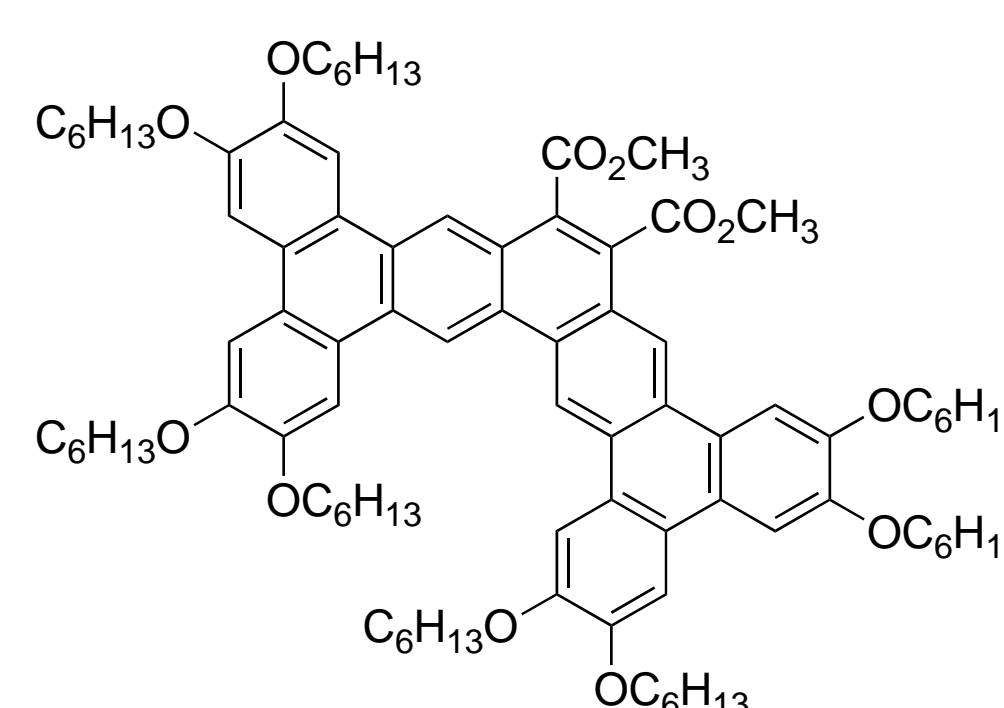
Cyclotrimerization of polycyclic arynes afford extended or sterically congested complex PAHs with fascinating structures, of theoretical and/or practical interest.



As a recent example we have synthesized hexabenzotrianthrycene (**cloverphene**), the largest *cata*-condensed PAH that has been prepared to date.

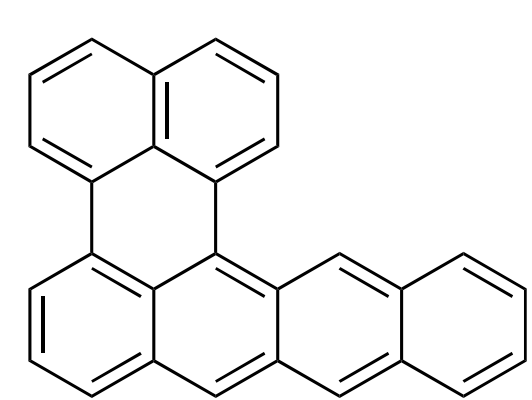
Liquid crystals:

Multifunctional discotic liquid crystals made by Pd-catalyzed cycloaddition of functionalized triphenylene with DMAD.^[4]

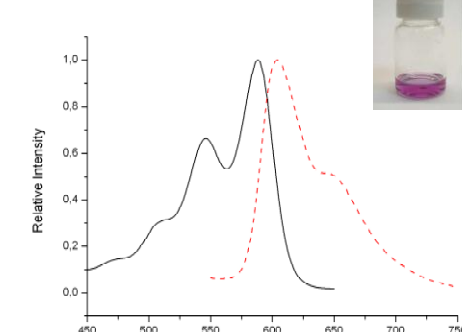


Molecular electronics:

Cycloaddition reactions of arynes with appropriate oligofurans afford novel perylene derivatives with electronic properties which make them potential organic semiconductors.^[5]

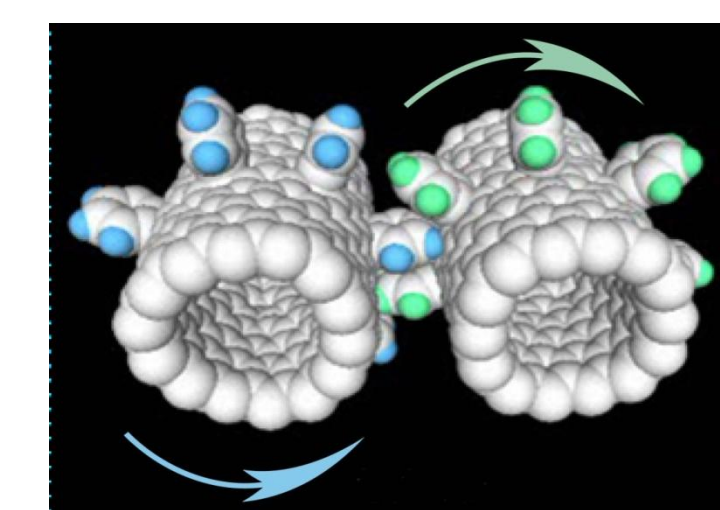


$Ga_{\text{POMO-LUMO}} = 2.1 \text{ eV}$



Functionalization of carbon nanotubes:

- to improve solubility and processability
- to modify the electronic properties
- towards the fabrication of molecular machines



[1] D. Peña, S. Escudero, D. Pérez, E. Guitián, L. Castedo *Angew. Chem. Int. Ed.* **1998**, *37*, 2804. [2] D. Peña, D. Pérez, E. Guitián, L. Castedo *J. Am. Chem. Soc.* **1999**, *121*, 5827. [3] E. Guitián, D. Pérez, D. Peña, in *Topics in Organometallic Chemistry*; Tsuji, J., Ed.; Springer-Verlag: Weinheim, 2005; Vol. 14, pp. 109-146. [4] C. Romero, D. Peña, D. Pérez, E. Guitián, R. Termine, A. Golemme, A. Omenat, J. Barberá, J. L. Serrano *J. Mater. Chem.* **2009**, *19*, 4725-4731. [5] A. Criado, D. Peña, A. Cobas, E. Guitián, *Chem. Eur. J.* **2010**, in press