

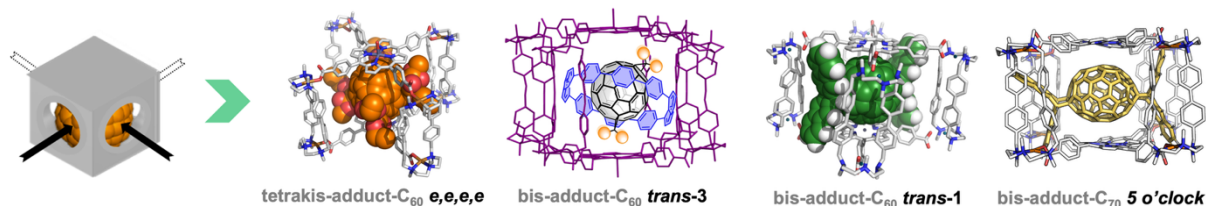
Multipurpose Porphyrin-Based Supramolecular Nanocapsules for Chemistry at the Confined Space

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The design of a confined cavity dictates the type of guest to be encapsulated, and supramolecular cages are tunable scaffolds that allow the rational design of their cavities. Targeting fullerenes as guests, their regioselective functionalization and the control of the number of adducts are highly important to unlock the development of fullerene chemistry. Nowadays, easy-accessible C₆₀ and C₇₀ fullerene mono-adducts are mainly used in any application[1] due to the hampered accessibility to pure alternative fullerene poly-adduct derivatives. In general, multi-adduct mixtures with uncontrolled regioselectivity (multi-isomers) are obtained, and chromatographic purification is too costly and time-consuming. Herein, porphyrin-based supramolecular nanocapsules[2,3] are used as supramolecular shadow masks to tame the over-reactivity of Bingel-Hirsch-type cyclopropanation reactions and, more importantly, to have full control over the equatorial regioselectivity and the number of additions. Thus, exclusively equatorial bis-, tris- and tetrakis-C₆₀ adducts using ethyl-bromomalonate are stepwise obtained and fully characterized (NMR, UV-vis and XRD). Furthermore, the regioselectivity control is finely tuned using a three-shell Matryoshka-like assembly towards synthesizing a single trans-3 bis-Bingel-C₆₀ for the first time.[4] Also, the mask strategy is extended to Diels Alder reactions with full control of the regioselectivity in the synthesis of trans-1 bis-pentacene-C₆₀. [5] These results, recently extended to C₇₀, [6,7] are fully attributed to the confinement control imposed by the capsule's cavity, and represent a novel and unique strategy to infer regio-control to the synthesis of fullerene multi-adducts. We envision that the described protocol will produce a plethora of derivatives for applications such as solar cells. We will also discuss the selective purification of fullertube mixtures and the encapsulation of photo-active guests.

Supramolecular Masks



References

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