Stereoelectronic control of alkyne cyclizations and cycloadditions: towards precisely shaped and functionalized carbon nanostructures and faster click chemistry

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New chemical reactions open new opportunities for controlling life and matter at the molecular level. I will illustrate how one can use sequential chemical transformations from one of the simplest organic functional groups for solving two different problems: 1) bottom-up approaches to conjugated carbon nanostructures, and 2) faster bioorthogonal chemistry.

In the 1st part, I will outline cascade transformations for the bottom-to-top preparation of carbon nanostructures for molecular electronics (graphene nanoribbons). In our approach, alkyne chains of varying sizes, shapes and functionalities, are built in a modular fashion and “zipped” up into graphene substructures via controlled radical polymerization. The success of this approach is based on the newly redesigned rules for alkyne cyclizations.

Graphene nanoribbons:

In the 2nd part, I will discuss selective Transition State stabilization in the design of non-catalyzed alkyne-azide cycloadditions for bioorthogonal chemistry. Paradoxically, this approach promises the click reagents which are more stable but also more reactive than strained cycloalkynes.