

Nonperturbing, conjugation-preserving covalent functionalization of single-walled carbon nanotubes

Antonio Setaro¹, Mareen Gläske, Mohsen Adeli², Rainer Haag², and Stephanie Reich¹

¹ Physics Department, Free University Berlin, 14195 Berlin, Germany

² Chemistry Department, Free University Berlin, 14195 Berlin, Germany

The most common outcome of covalent treatments of carbon nanotubes is the conversion of sp^2 carbon atoms into their sp^3 hybridization state. Even mild approaches interrupt the conjugation of the carbon network with detrimental effects on their optoelectronic properties. Cycloaddition reactions establish covalent bonds through π -electrons to bridge targeted functionalities onto the tubes. The carbon atoms below the bridge are converted into the sp^3 state (closed configuration, Fig. 1a) or, if the C-C bond below the bridge is released, keep their sp^2 character (open configuration, Fig. 1b) and preserve the overall conjugation of the extended network. We have recently demonstrated that the outcome of a triazine-based [2+1] cycloaddition reaction results in the open configuration (Fig. 1c) and preserves the intrinsic properties of the tubes, even at high degrees of functionalization (4%) [1]. Here we will highlight some of the benefits of this approach, such as the preservation of their radiative emission (Fig. 1d) or the fine-tuning of the position of their Fermi levels.

We will moreover discuss how the functionalized tubes can be exploited as starting platform for advanced materials. We show how the attachment of molecular systems makes them integrating part and in electronic communication with the conjugated network of the tubes, yielding new ways to non-perturbatively tailor, control, and alter the optical response of the tubes for novel applications. The conjugation of the molecular switch spyropiran-merocyanine, for example, enables controlled on-off switching of the tubes' emission to be exploited for nanotubes-based super-resolution microscopy.

[1] A. Setaro, *et al.*, Nat. Comm. **8**, 14281 (2017).

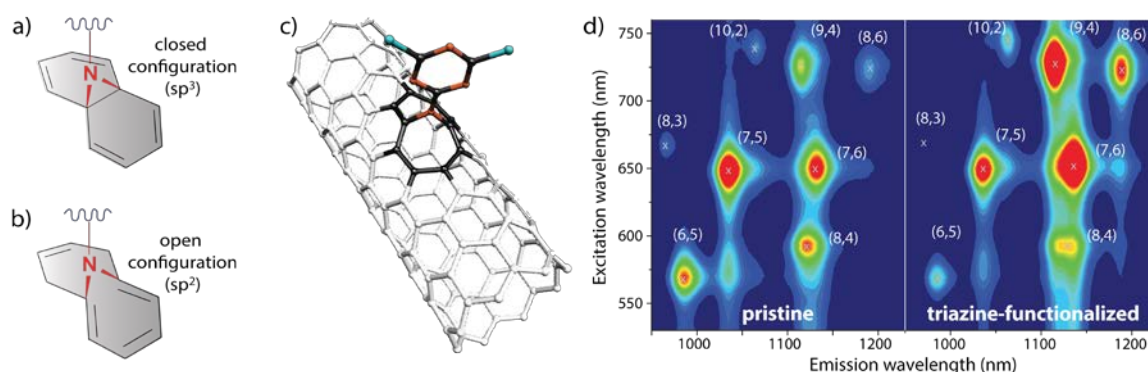


Fig.1 As a product of a [2 + 1] cycloaddition reaction bridging a triazine molecule, the two carbon atoms underlying the bridge can be in (a) their sp^3 state in the closed configuration, or (b) their sp^2 state in the open configuration. (c) Quantum chemical calculations show that the open configuration is the stable one. (d) Comparison between the PLE chart of pristine and triazine functionalized tubes.