

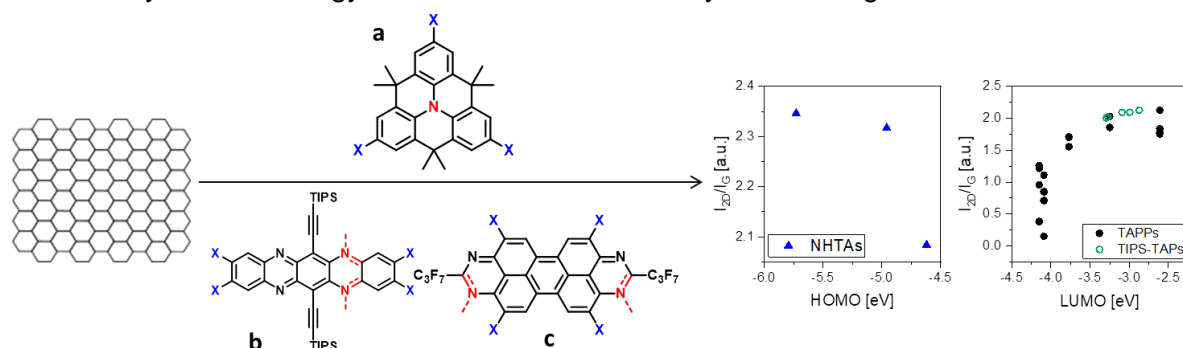
# Investigation of donor/acceptor relation for non-covalent Graphene doping using *N*-Heteropolycycles

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In recent years, non-covalent functionalization of graphene with organic molecules has attracted considerable attention due to the possibility of controlled chemical doping. Graphene shows strong  $\pi$ - $\pi$  interactions with aromatic molecules allowing the deposition of a range of organic materials from solution with scope for molecular self-assembly<sup>[1]</sup>. However, a number of aspects have not been sufficiently addressed, for example, it is unclear in which way the periphery around the aromatic core and potentially pre-organization of the molecules prior to deposition has an impact on supramolecular arrangement and packing density on the surface. In addition, it is particularly difficult to quantitatively relate the doping strength to the donor/acceptor properties of the molecules, as molecular packing (governed by the overall structure of the molecule) has to be decoupled from electronic properties (governed by the aromatic core).

In our study we use different classes of *N*-Heteropolycycles for the non-covalent functionalization of CVD graphene with the aim to fundamentally shine light on chemical doping and surface modification. This class of organic molecules is especially suitable, as the structure can be systematically varied. In particular, the donor/acceptor strength can be varied via the substitution pattern of the core and thus tuned independently from the molecular periphery. We focus on a series of derivatives of tri-isopropylsilyl-Tetraazapentacene<sup>[2]</sup> (TIPS-TAPs), Tetraazaperopyrene<sup>[3]</sup> (TAPPs) and *N*-Heterotriangulenes<sup>[4]</sup> (NHTAs) to investigate the impact of different molecular structures on the electronic and surface properties of graphene to understand how to precisely tune graphene to the different needs in electronic applications, without altering its lattice structure. Raman spectroscopy (in combination with AFM/KPFM) is a particularly versatile characterization technique, as both doping and packing density of the molecule can be evaluated simultaneously. Additionally surface energy values can be extracted by contact angle measurements.



**Figure 1:** Deposition of different *N*-Heteropolycycles ( **a**: NHTAs, **b**:TIPS-TAPs, **c**: TAPPs) leading to changes in graphene Raman intensity ratio  $I_{2D}/I_G$  (= Fermi level) depending on the donor/acceptor strength of the molecules, represented by their HOMO/LUMO energies.

Our studies show that the observed changes in electronic structure of graphene are primarily affected by the electronic structure of the molecules themselves, as long as the used substituents are comparable in their steric effects. For acceptor-type molecules, (e.g. TAPPs and TIPS-TAPs) a correlation between LUMO energy of the molecules and Fermi level shift in graphene is observed independent of how much molecule is deposited. For donor-type molecules (e.g.) NHTAs a similar correlation involving the HOMO energy can be seen. The Raman data is supported by changes in the work function. Surface energy values could only be measured for the TAPPs, since the other molecules are partially removed through solvents involved in contact angle measurements.

## Reference

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[2] *Angew. Chem. Int. Ed.* **2013** 52, 3810 – 3821.

[3] *Chem. Eur. J.* **2015** 21, 17691.

[4] *Chem. Rec.* **2015** 15, 1119–1131.