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Donor/acceptor relation for non-covalent chemical doping of graphene using *N*-Heteropolycycles

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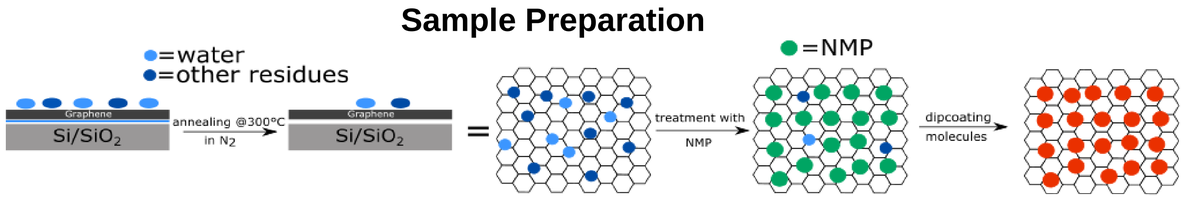
Motivation

N-Heteropolycycles: Molecular building blocks of outstanding versatility

Graphene: Substrate with unique optical and electronic properties

- Does the doping of graphene correlate with the donor/acceptor strength of the molecule?
- Is it possible to have doping and work function modification tuned independently from each other, or to which extent are they intrinsically coupled?

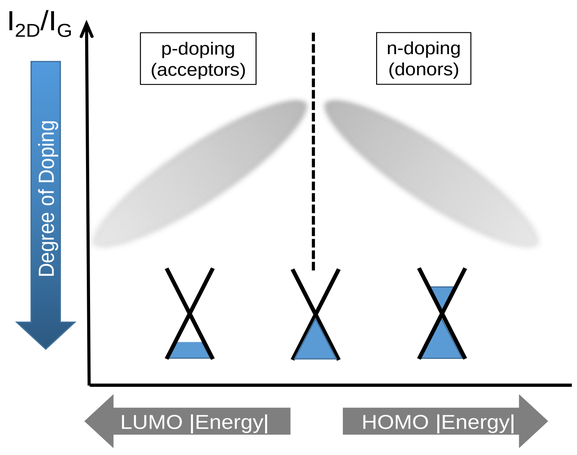
Sample Preparation



Raman + KPFM

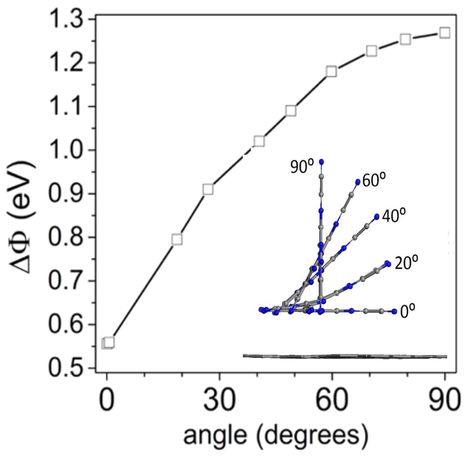
Fingerprints of Doping

Expectation based on electronic grounds



[1] Nature Nanotechn. 2008, 3, 210.

Molecule orientation



[2] J. Phys. Chem. C 2014, 118, 4784−4790

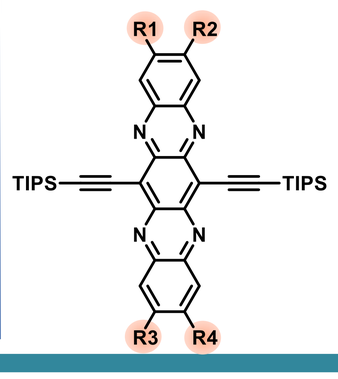
Molecules

Tetraazapentacene-Derivatives, (TIPS-TAPP)
Bunz Group, Uni Heidelberg

Tetraazaperopyrene-Derivatives (TAPP),
Gade Group, Uni Heidelberg

Triangulene-Derivatives,
Kivala Group, Uni Heidelberg

TIPS-TAP- weak acceptors



R1/2/3/4 = H (4H)

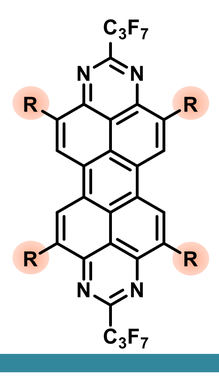
R1 = Br, R2/3/4 = H (1Br)

R1/2 = Br, R3/4 = H (2Br)

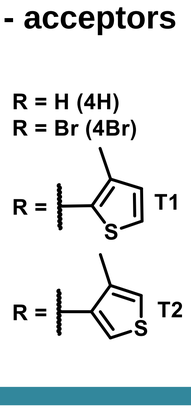
R1/2/3/4 = Br (4Br)

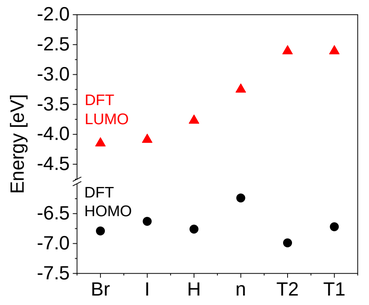
R1/2/3/4 = I (4I)

TAPP - acceptors



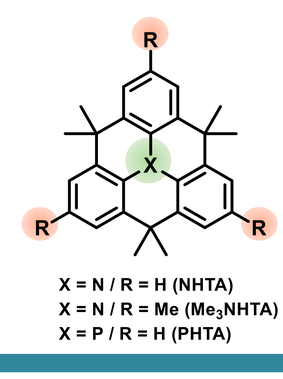
R = H (4H)
R = Br (4Br)





Example of variation in acceptor strength by substitution pattern

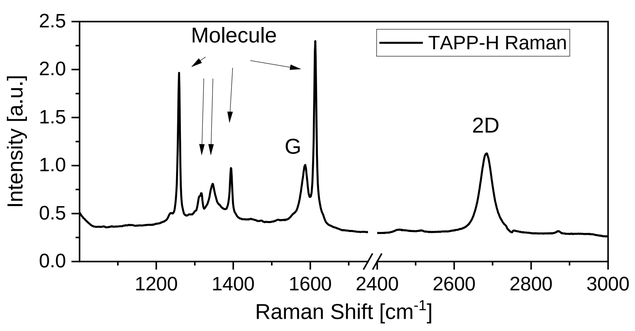
Triangulenes- donors

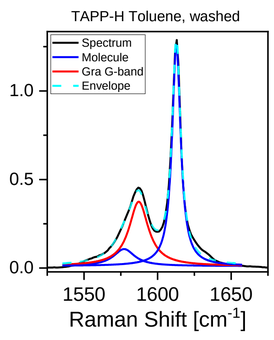


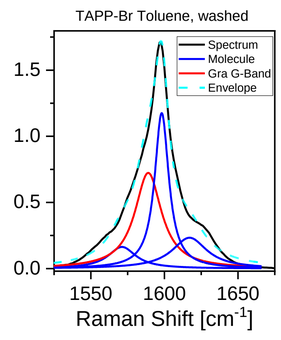
X = N / R = H (NHTA)
X = N / R = Me (Me_3NHTA)
X = P / R = H (PHTA)

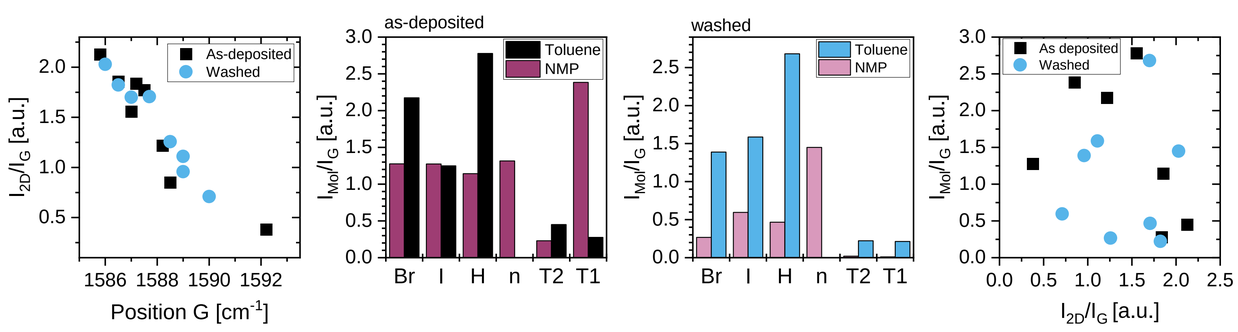
Results Raman Spectroscopy

Example TAPP derivatives



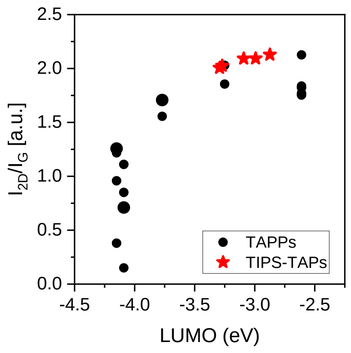


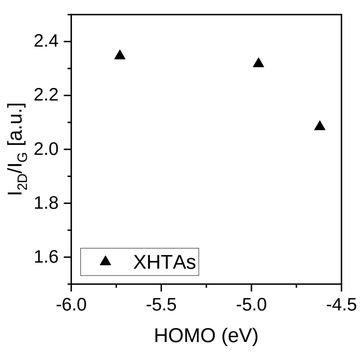




- Deposition of molecule results in changes of graphene 2D/G intensity ratio and G-band shifts which can be extracted from fitting due to **doping**
- **Density of molecule** per area qualitatively approximated as relative intensity of molecular vibration (I_{Mol}/I_G) **can be tuned** by deposition conditions
- **No correlation of 2D/G with number of molecules per area**

Acceptors

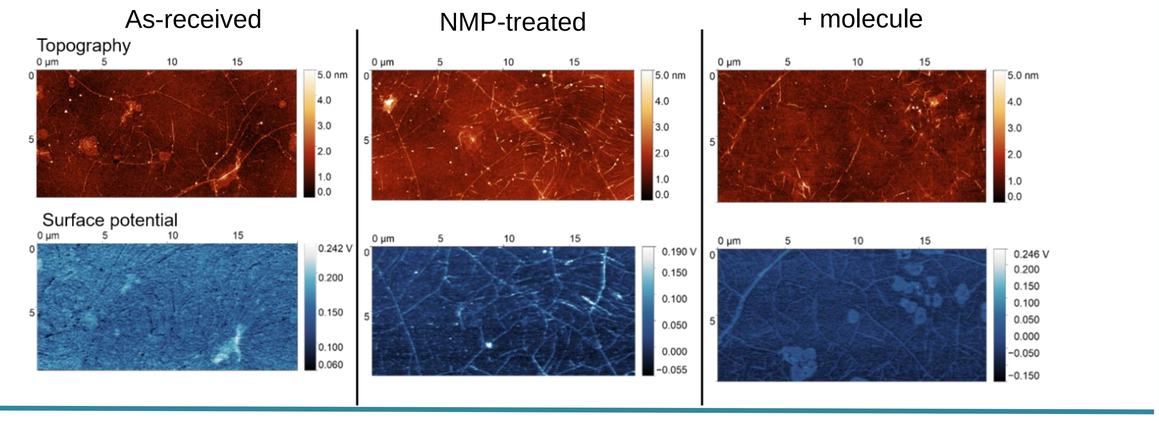




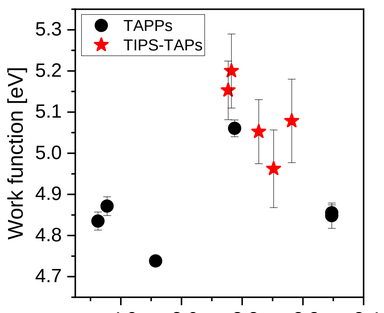
Donors

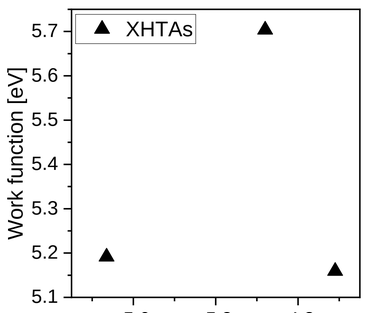
- **Doping level scales with donor/acceptor strength** irrespective of molecular packing density; steep increase in doping strength for LUMO < -4.5 eV
- Data from TAPP and TIPS-TAP fall on the same curve in spite of different molecular architecture (e.g. bulky substituents in TIPS-TAP) which will impact arrangement on substrate

Results Kelvin-Probe-Force Microscopy



Acceptors





Donors

- Unintuitive correlation due to the manifold of different molecular structures and substituents; e.g. only for weak-medium acceptors (DFT LUMO -2.5 to -3.3 eV) work function increases with increasing acceptor strength as would be expected based on electronic grounds
- **Independent variation of doping level and work function in principle accessible**

Conclusion

- The wide variety of *N*-Heteropolycycle derivatives with modified substitution patterns allows to **rationalise fundamentals of chemical doping** through noncovalent functionalisation
- Degree of doping is controllable via engeneering of HOMO/LUMO levels of dopants, with **very little influence of molecule packing density**
- Additional surface dipole effects are working against a controlled tuning of doping level and work function at the same time → independent variation of doping level and work function