

# Doped Polycyclic Hydrocarbons for Nanoelectronics and Energy Conversion

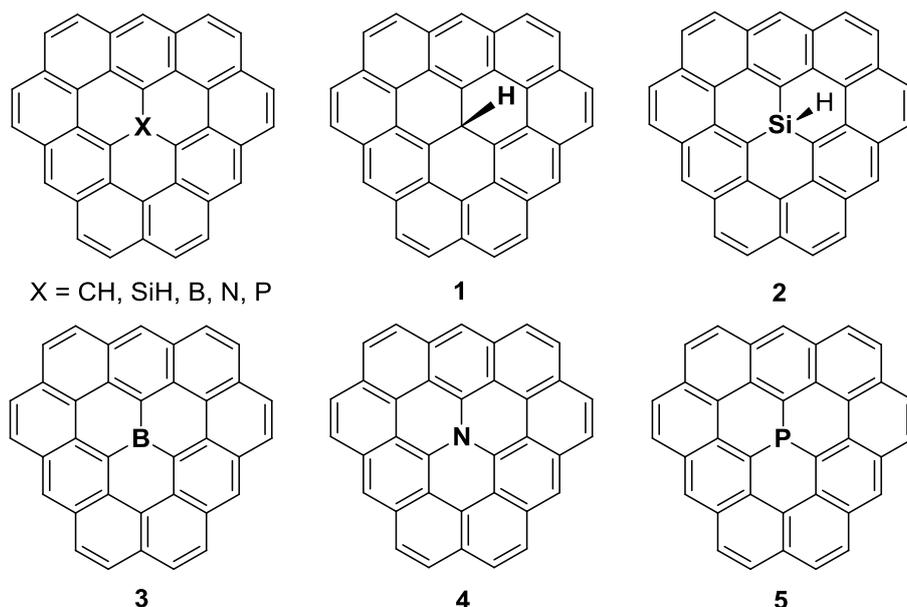
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Polycyclic aromatic hydrocarbons (PAHs) are typical organic semiconductors with interesting properties for many (nano-) electronics applications and for photovoltaics. [1] On the other hand, PAHs in the infinite size limit represent the “miracle material” graphene. However, in contrast to the “finite-size” nanoscale PAHs, graphene has no band gap and opening a band gap in graphene is a challenging task that must be solved for semiconducting technologies including nanoelectronics based on graphene. [2] One way to open a band gap is internal doping of graphene. [2]

Thus, we have recently studied the effect of internal doping on the properties of PAHs by performing calculations with density functional theory (DFT) and semiempirical configuration interaction methods on a series of doped PAHs **1–5** with the dopants X = CH, SiH, B, N, and P (see Figure). [1] Such calculations also serve to model and understand the effects of internal doping in graphene.



Adiabatic and vertical electron affinities and ionization potentials, optical and transport band gaps and exciton binding energies were calculated for **1–5** based on the DFT, time-dependent (TD) DFT and semiempirical unrestricted natural orbital–configuration interaction singles (UNO–CIS) methods. [1] In addition, we have estimated the chemical reactivity of **1–5** by calculating their aromaticity and diradical characters. [1] Photoinduced electron transfer in complexes of **1–5** with fullerene C<sub>60</sub> and porphyrin was also shown to be plausible with the above methods. [1] We have determined that dopants can be classified into three groups based on the results of our calculations: 1) CH- and P-dopants, which interact weakly with the  $\pi$ -system, 2) SiH-dopant, which interacts weakly with the  $\pi$ -system, but strongly deforms the planar PAH skeleton and therefore changes its electronic properties, and 3) B- and N-dopants, which interact strongly with the  $\pi$ -system, although they influence the electronic properties in opposite directions. [1]

[1] P. O. Dral, M. Kivala, T. Clark, *J. Org. Chem.*, **2012**, ASAP, DOI: 10.1021/jo3018395.

[2] X. F. Fan, Z. X. Shen, A. Q. Liu, J. L. Kuo, *Nanoscale*, **2012**, 4, 2157-2165.