

Impact of crosslinks, curvature and radical character on the optical band gap of nanographenes

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In this work, the optical band gaps of nanographenes or polycyclic aromatic hydrocarbons (PAHs) are computed using time-dependent density functional theory with a variety of different functionals being benchmarked against OBGs measured by ultraviolet-visible spectroscopy. TD-DFT calculations using the best performing functional (HSE06) are compared to experimental results for a range of PAHs. Further computational calculations are performed on larger PAHs, including molecules consisting of crosslinking between PAHs, curved PAHs and PAH with radical character. Crosslinks cause a small decrease in the OBG of the monomers which saturates after 3-4 crosslinks. Curvature in PAHs is shown to increase the optical band gap due to the resulting change in hybridisation of the system, but this increase saturates at higher curvatures. The increase in OBG between a flat PAH and a highly strained curved one is shown to be equivalent to a difference of several rings in size for peri-condensed aromatic systems. The effect of sigma radicals on the optical band gap was also shown to be negligible, however, π -radicals were found to decrease the band gap by ~ 0.5 eV. These findings have applications in understanding the molecular species involved in soot inception and for tuning the electronic properties of nanographenes for molecular electronics applications.

