

IMPACT OF CROSSLINKS, CURVATURE AND RADICAL CHARACTER ON THE OPTICAL BAND GAP OF NANOGRAHENES

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrogen terminated graphene fragments ubiquitous in nature with a rich chemistry. They have attracted interest due to their potential as graphene nanoribbons with tunable electronic structure¹, and their role as precursors for carbonaceous particulates in flames². However, how PAHs manage to form a condensed phase in flames is not well understood³. As such, measurements of properties such as the optical band gap (OBG) in flames are used to help shed light on what PAHs could play a role in nanoparticle formation. In this work, the OBGs of PAHs are computed using time-dependent density functional theory with a variety of different hybrid DFT functionals being benchmarked against OBGs measured by ultraviolet-visible spectroscopy. Further computational calculations are performed on larger PAHs, including molecules consisting of crosslinking between PAHs, curved PAHs and PAH with radical character to investigate the effect of such properties on the OBG and the impacts this has on electronic structure and the interpretation of OBG measurements.

Methods

The optical band gap of small PAHs were measured by means of ultraviolet-visible (UV-Vis) spectroscopy using the Agilent Cary spectrometer with cyclohexane as a solvent. Electronic structure calculations were performed using hybrid functional DFT at the HSE06/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, with the HOMO-LUMO gap taken as an estimate of the optical band gap for the PAHs.

Results and Discussion

Figure 1 shows the variance of OBG for flat, curved, radical, and cross-linked PAHs, and with the number of monomers for cross-linked PAHs. The results show that crosslinks cause a small decrease in the OBG but the effect saturates after 3-4 crosslinks, and is less significant as the monomer size increases. For flat, curved, and π -radical PAHs, the OBG follows a power-law decrease with the number of rings in the aromatic system. Comparing the results for pericondensed flat PAHs (yellow) and curved PAHs (purple), it is observed that curved PAHs tend to have a higher OBG compared to flat PAHs of the same size. It is also seen that this effect is more

significant when the PAHs are small and becomes less significant as the PAHs increase in size.

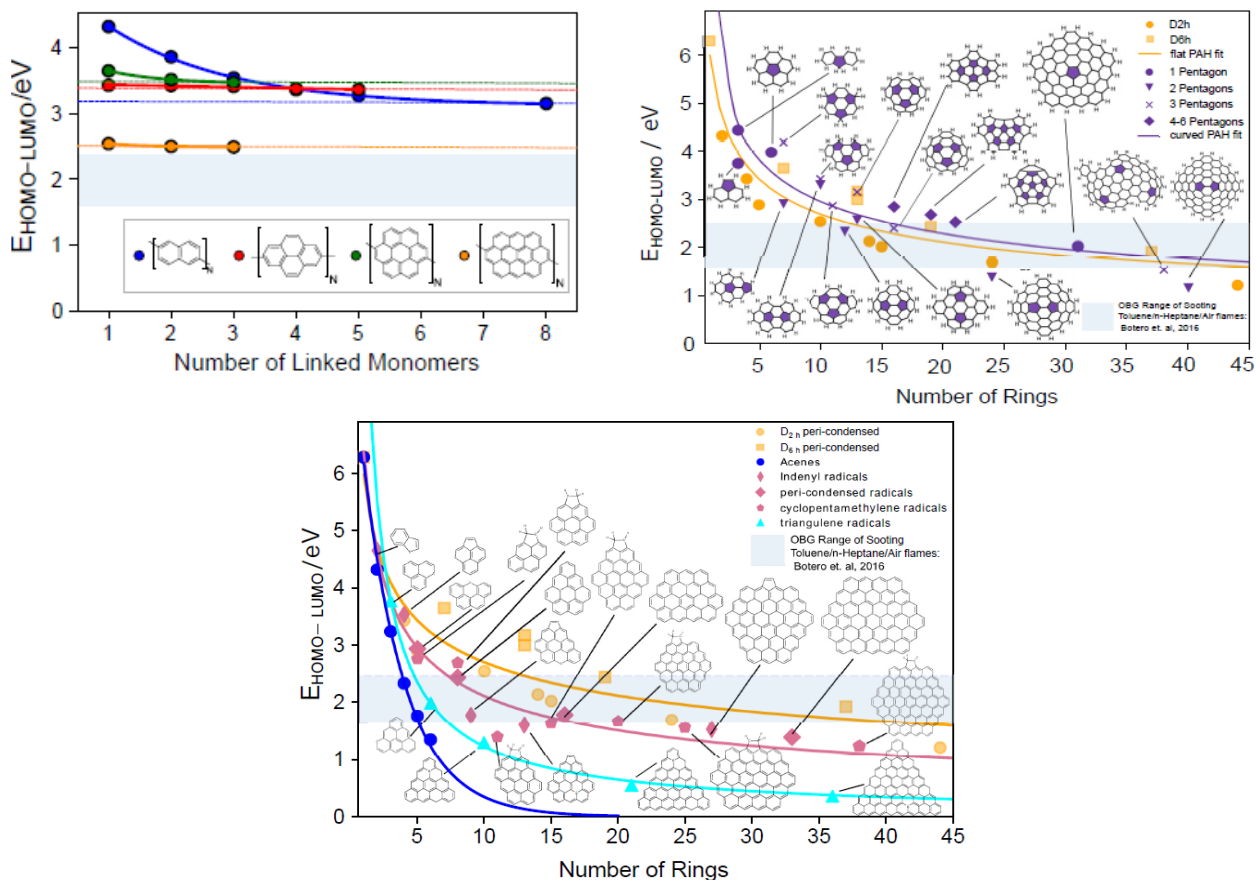


Figure 1. Variance in optical band gap with size for flat, curved, radical, and cross-linked PAHs.

In contrast, peri-condensed π -radical PAHs (magenta) are seen to have a lower OBG compared to flat peri-condensed PAHs, with the decrease being consistent across the size range at around 0.5 eV. These results have important implications for interpreting optical measurements in combustion diagnostics and in designing molecular electronics .

Conclusions

These results help identify the impact of complex features of PAHs, such as crosslinking, curvature, and radical character on their optical band gap.

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