CAMBRIDGE CARES

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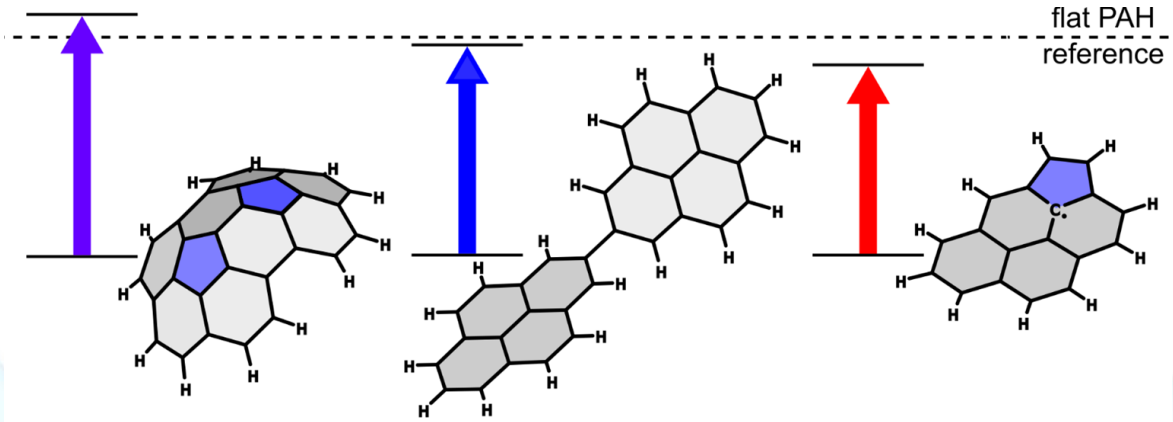
Impact of cross-links, curvature, and radical character on the optical band gap of nanographenes



July 18th , 2019

C4T

Cambridge Centre for Carbon Reduction in Chemical Technology

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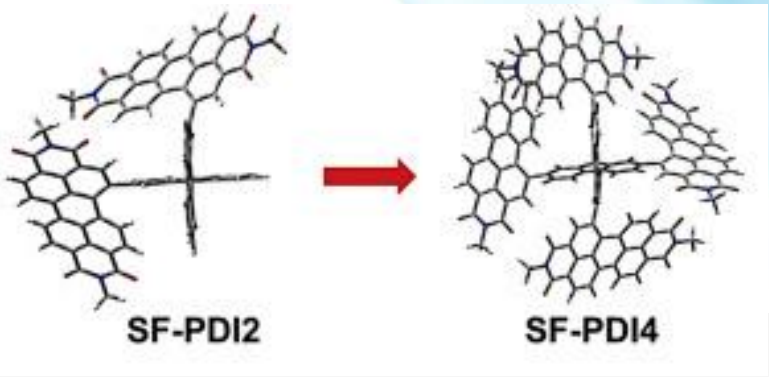
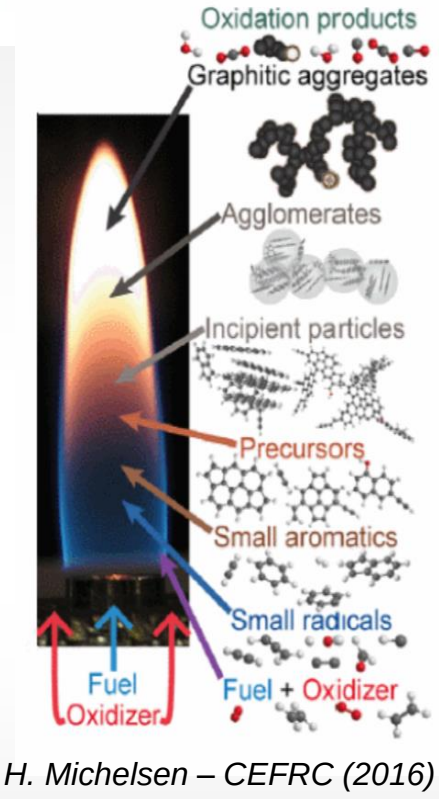
Motivations

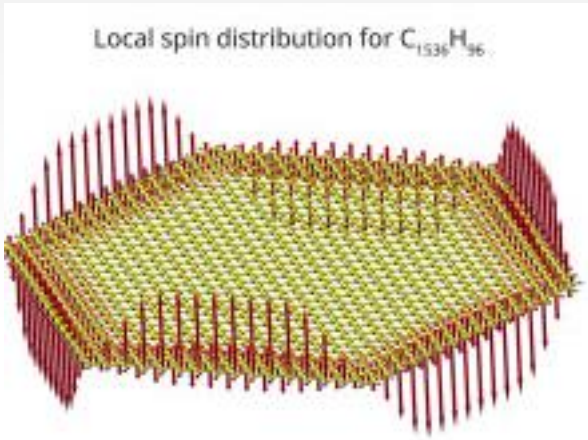
- Understanding what size graphene flakes form nanoparticles and are present in flames.
- Designing molecules for quantum dots, organic solar cells, and molecular electronics.



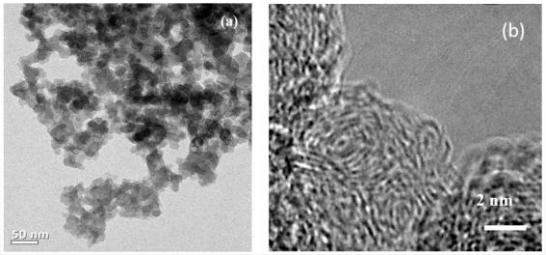
Yang, Lei, et al. *Journal of Power Sources* 324 (2016): 538-546.



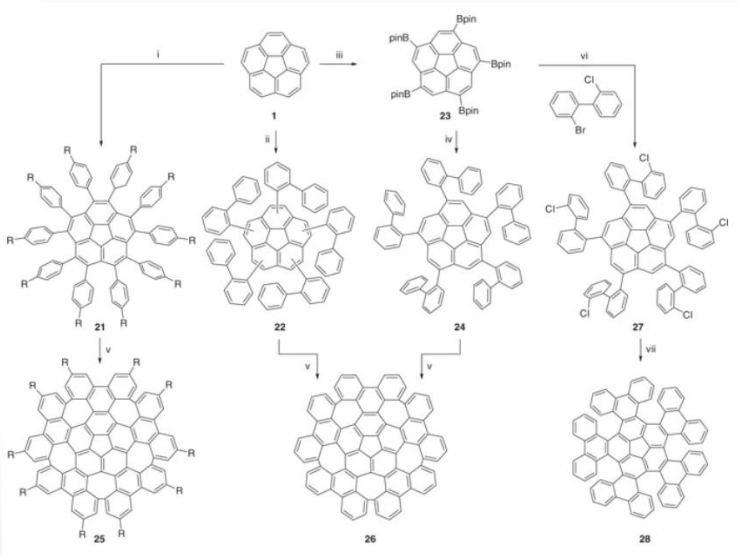
H. Michelsen – CEFRC (2016)



Ramos-Castillo, et al. *Carbon* (2019).

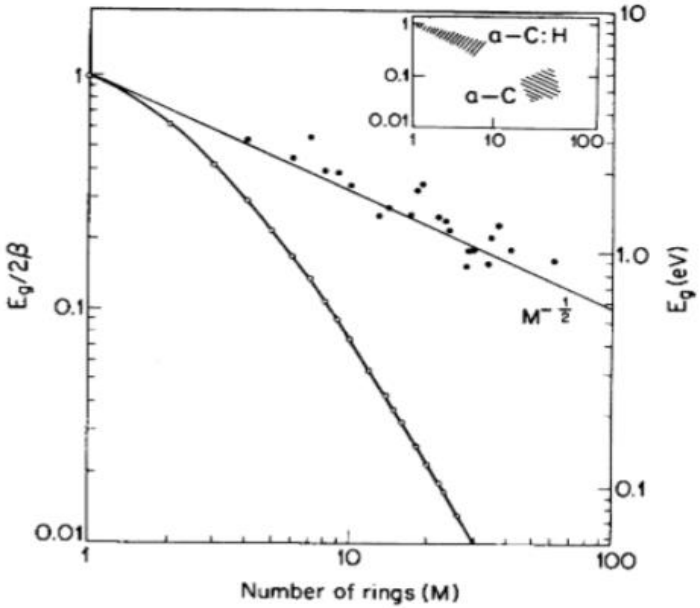


Kim, Dae-Yeong, et al. " *Nanomaterials* 9.5 (2019): 793.



Muzammil and Stuparu. Nature *Communications Chemistry* 2.1 (2019): 58.

Background



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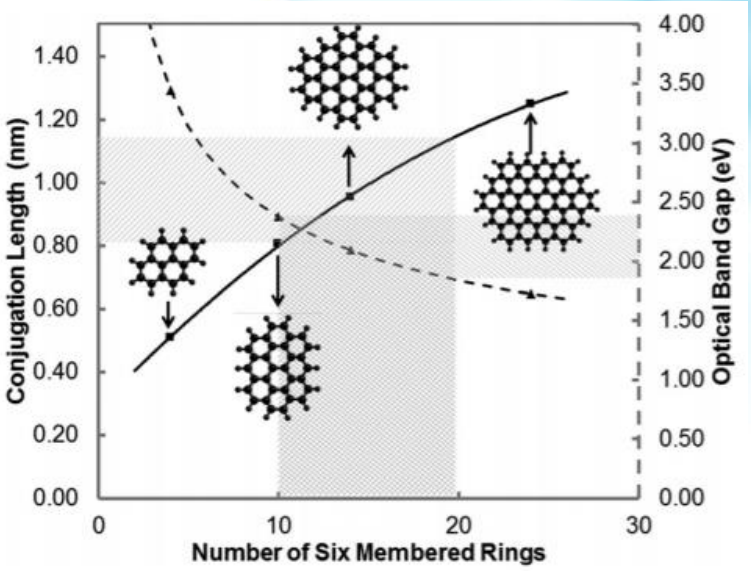
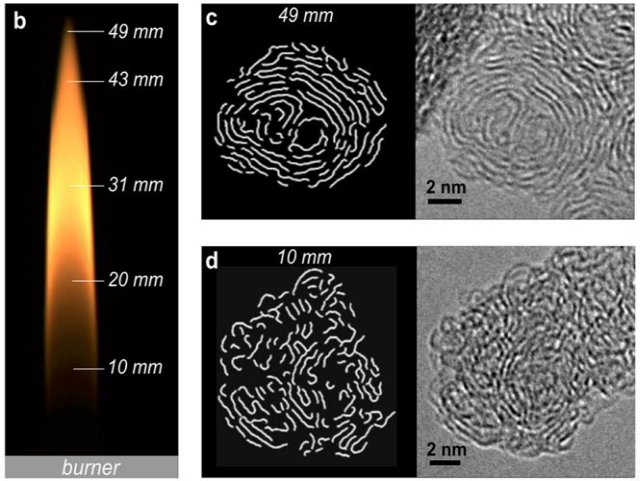
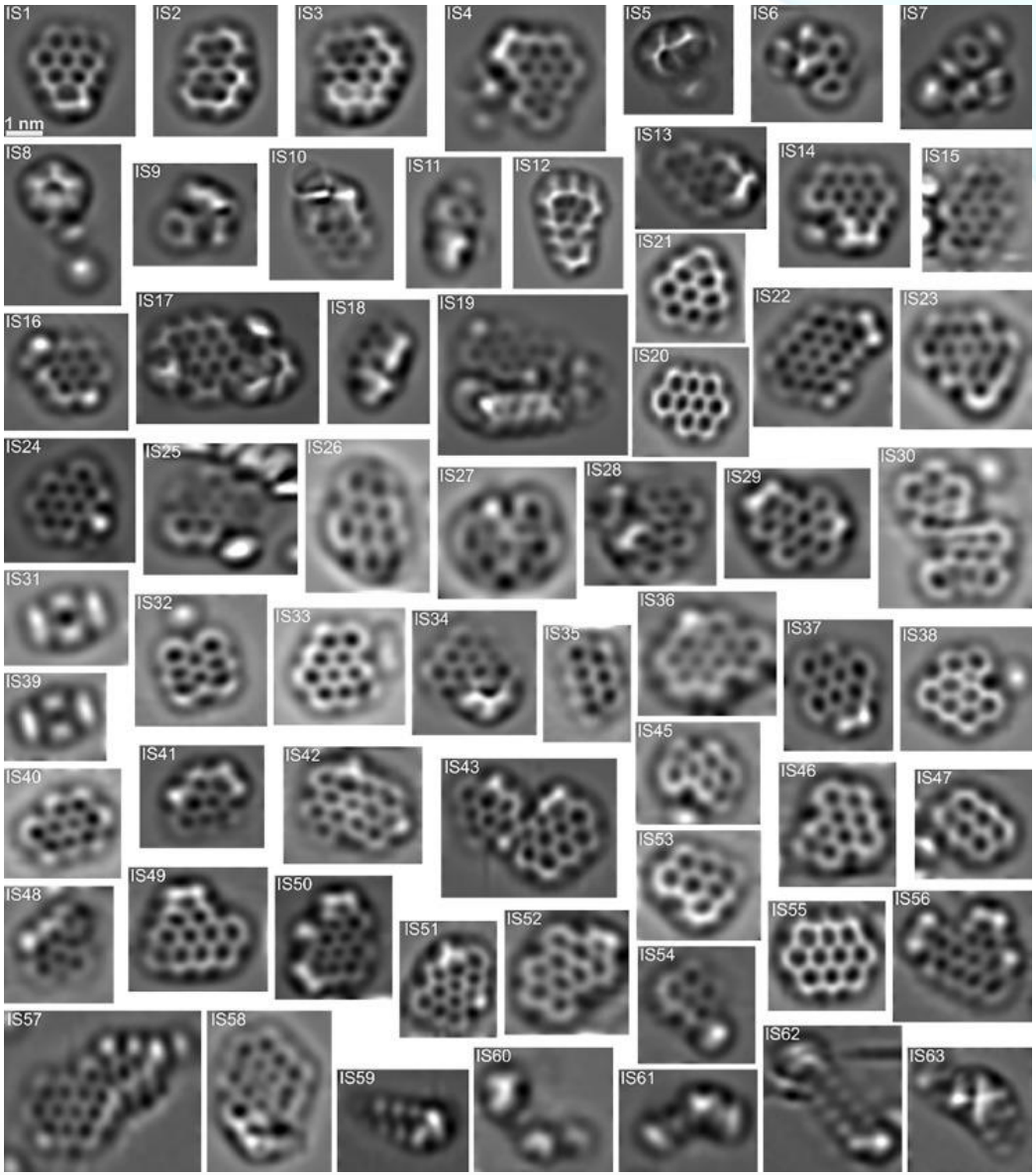


Adkins & Miller(2015). *Physical Chemistry Chemical Physics*, *17*(4), 2686-2695.



Martin, Jacob W., et al. *The Journal of Physical Chemistry C* 122.38 (2018): 22210-22215.



Commodo, Mario, et al. *Combustion and Flame* 205 (2019): 154-164.-

Key Questions:

What DFT methods are suitable for computing band gaps?

How is the optical band gap of nanographenes impacted by their structure?

What does this mean for combustion and carbon material applications?

Objectives:

Compute optical band gap for a variety of PAHs

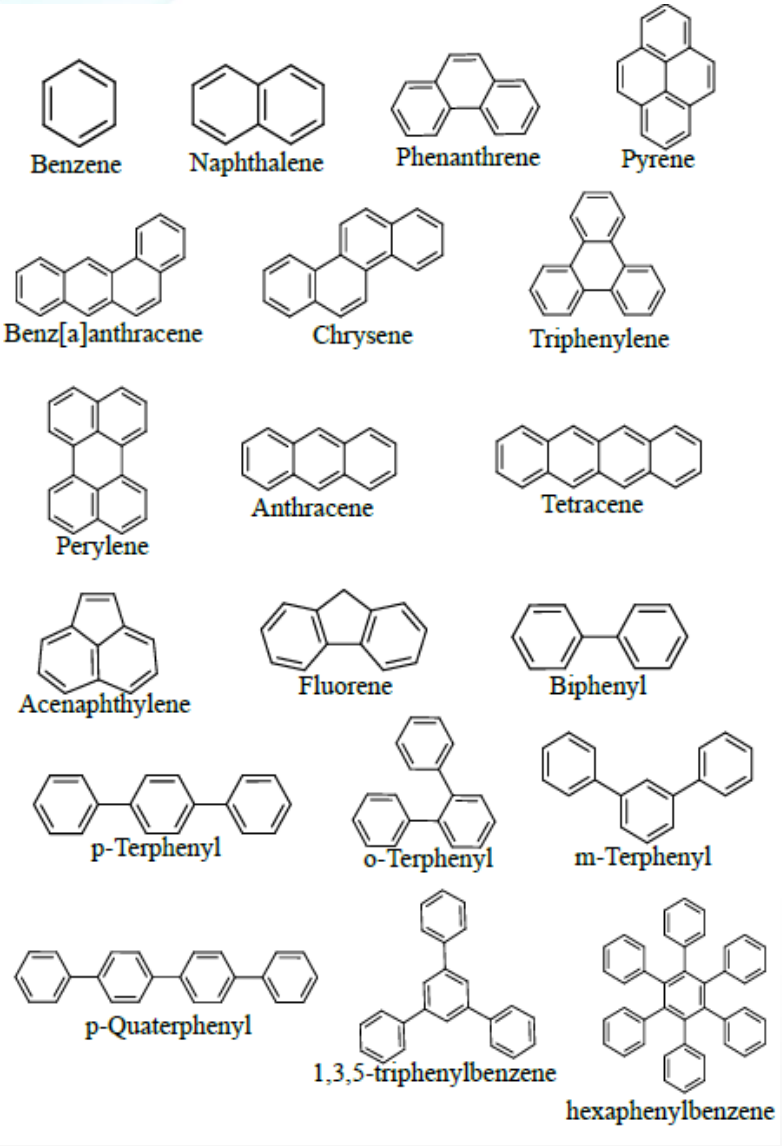
Determine

1) Impact of size, cross-linking, curvature, and radical character on OBG

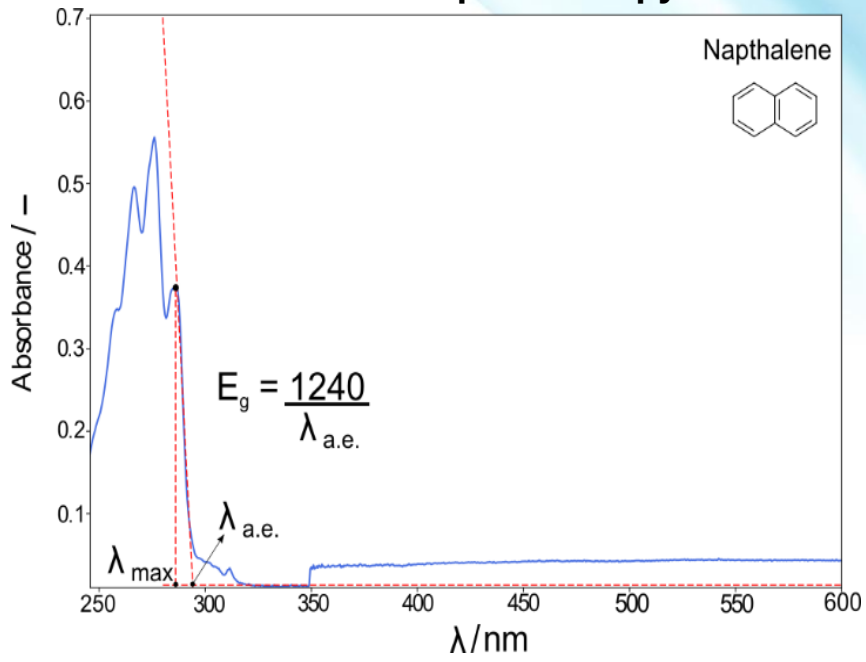
2) What this could mean for tuning carbon nanoparticles

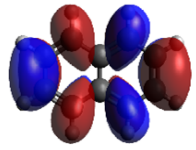
Methodology

Test Set of Molecules

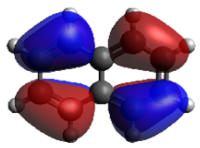


UV-Visible Spectroscopy

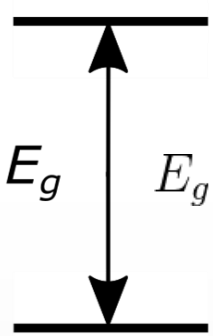




LUMO



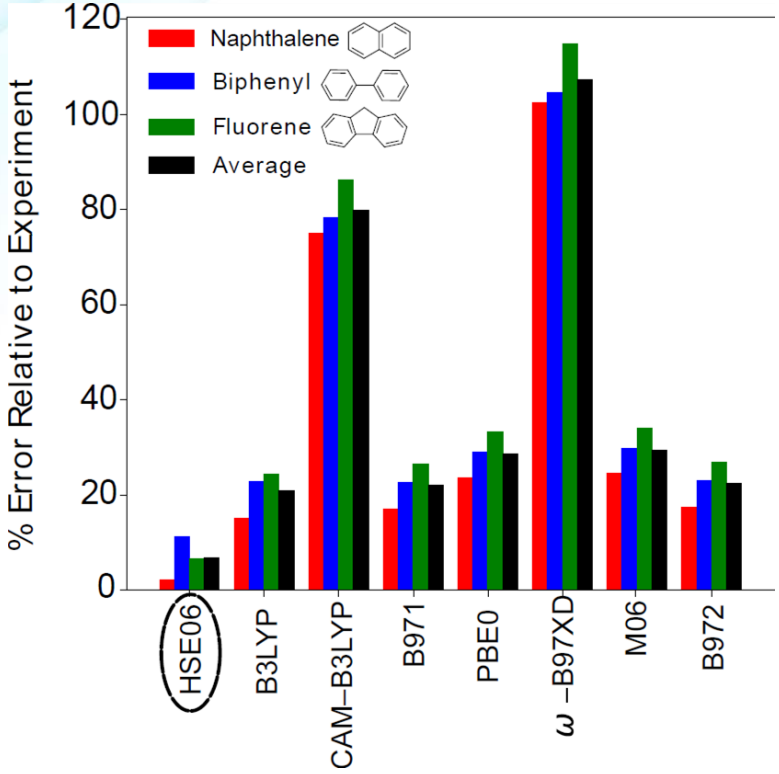
HOMO

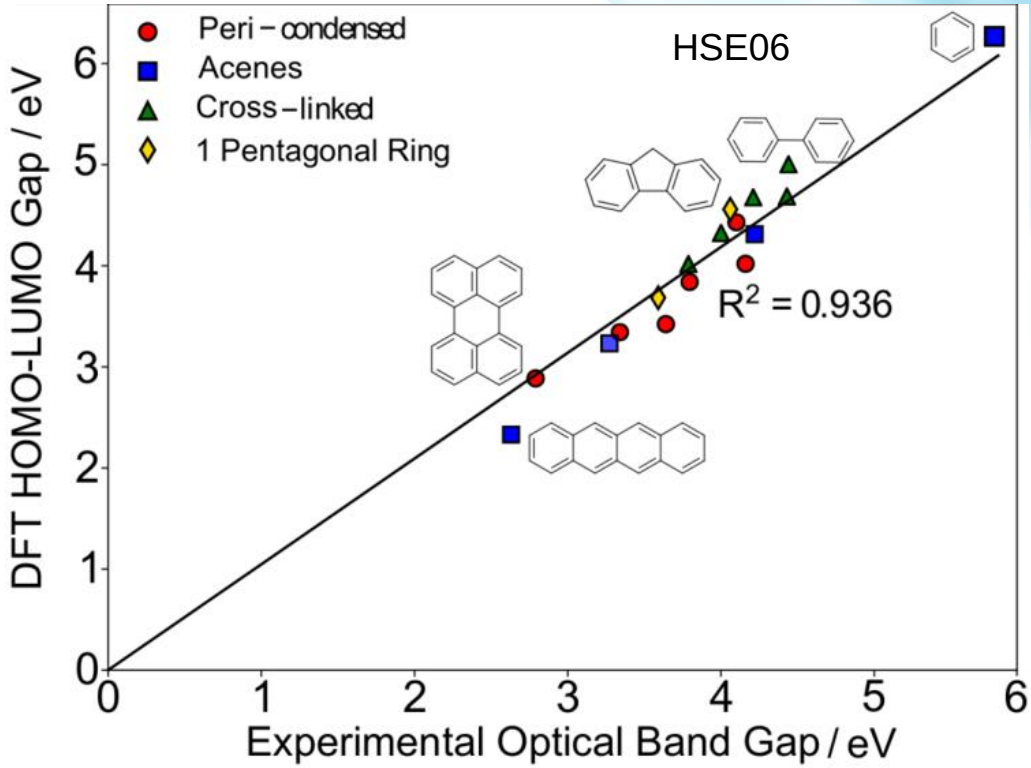


$$E_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$$

Computational Chemistry

Choosing a computational method

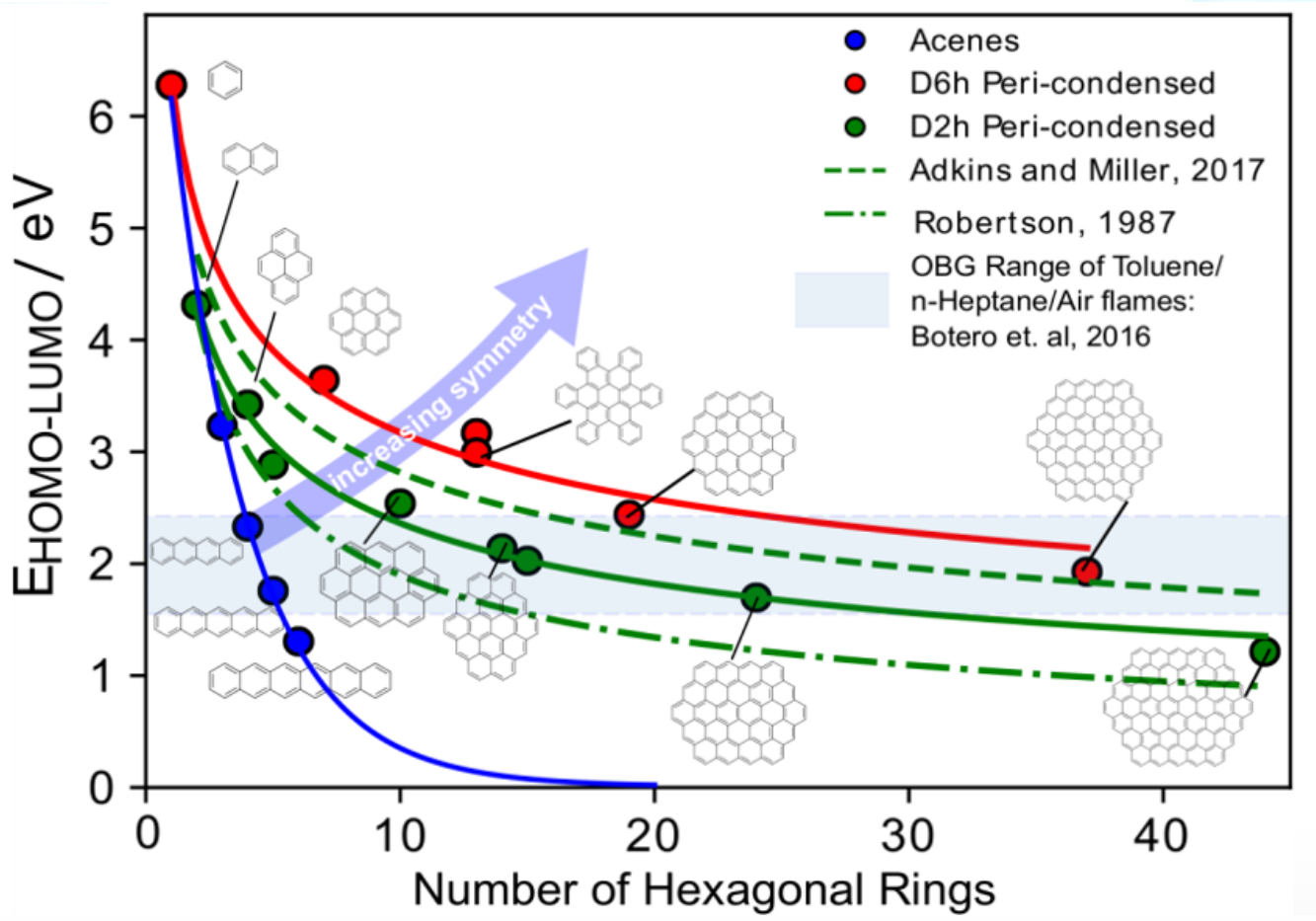




- Tested several popular computational chemistry methods based on density functional theory.

Certain DFT methods can reproduce experimental measurements

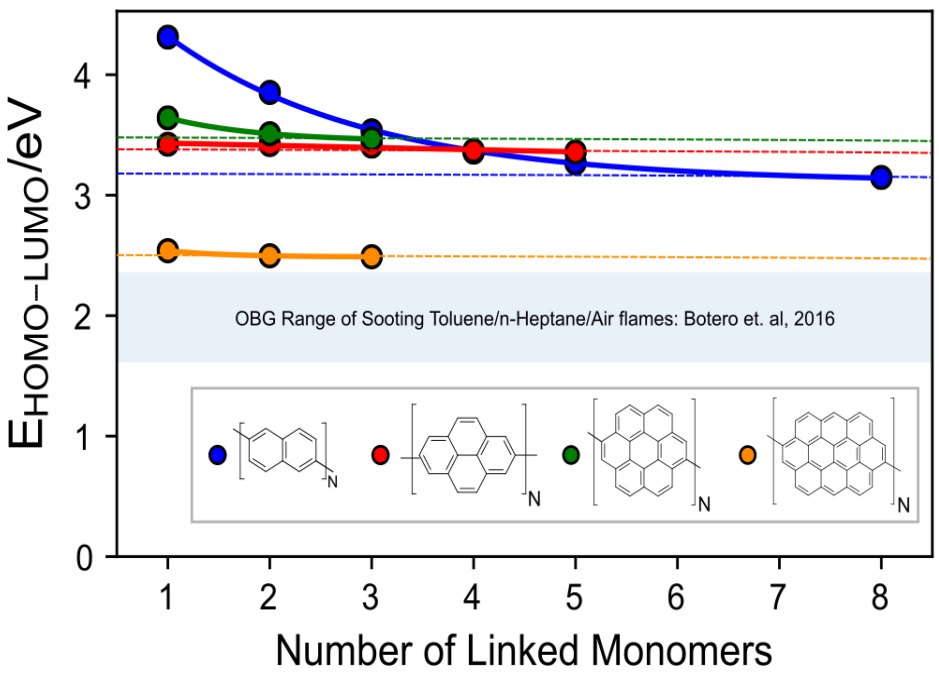
Traditional model nanographenes

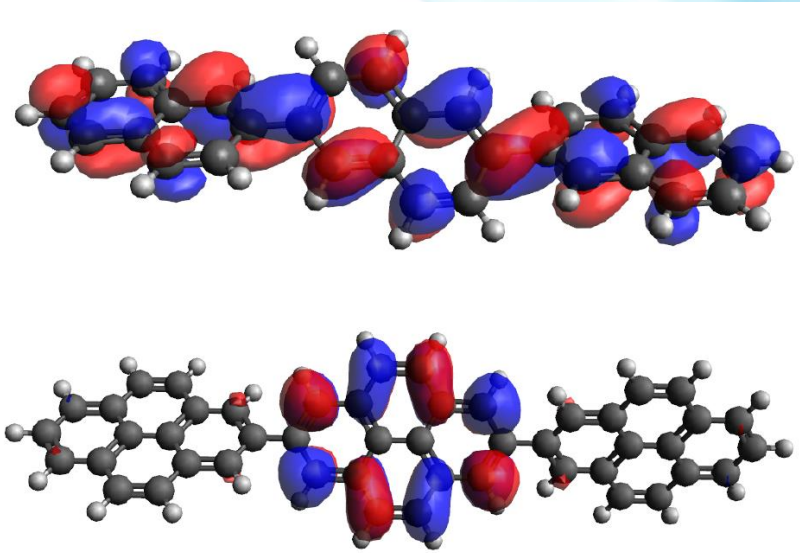


- All three groups approach a zero band gap limit
- In flames: 10 – 25 rings in size

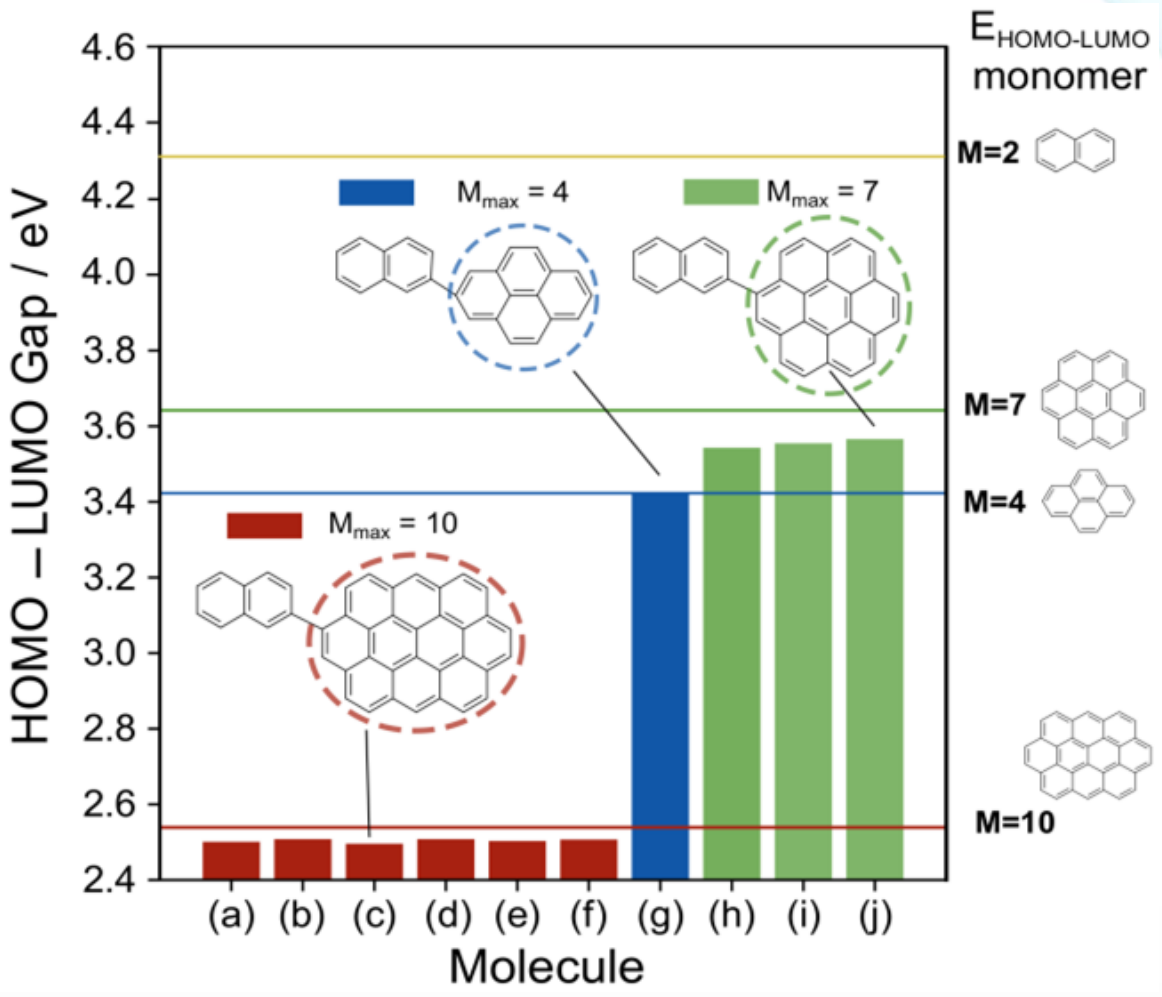
Size and symmetry of nanographene flake is key

Crosslinked Structures



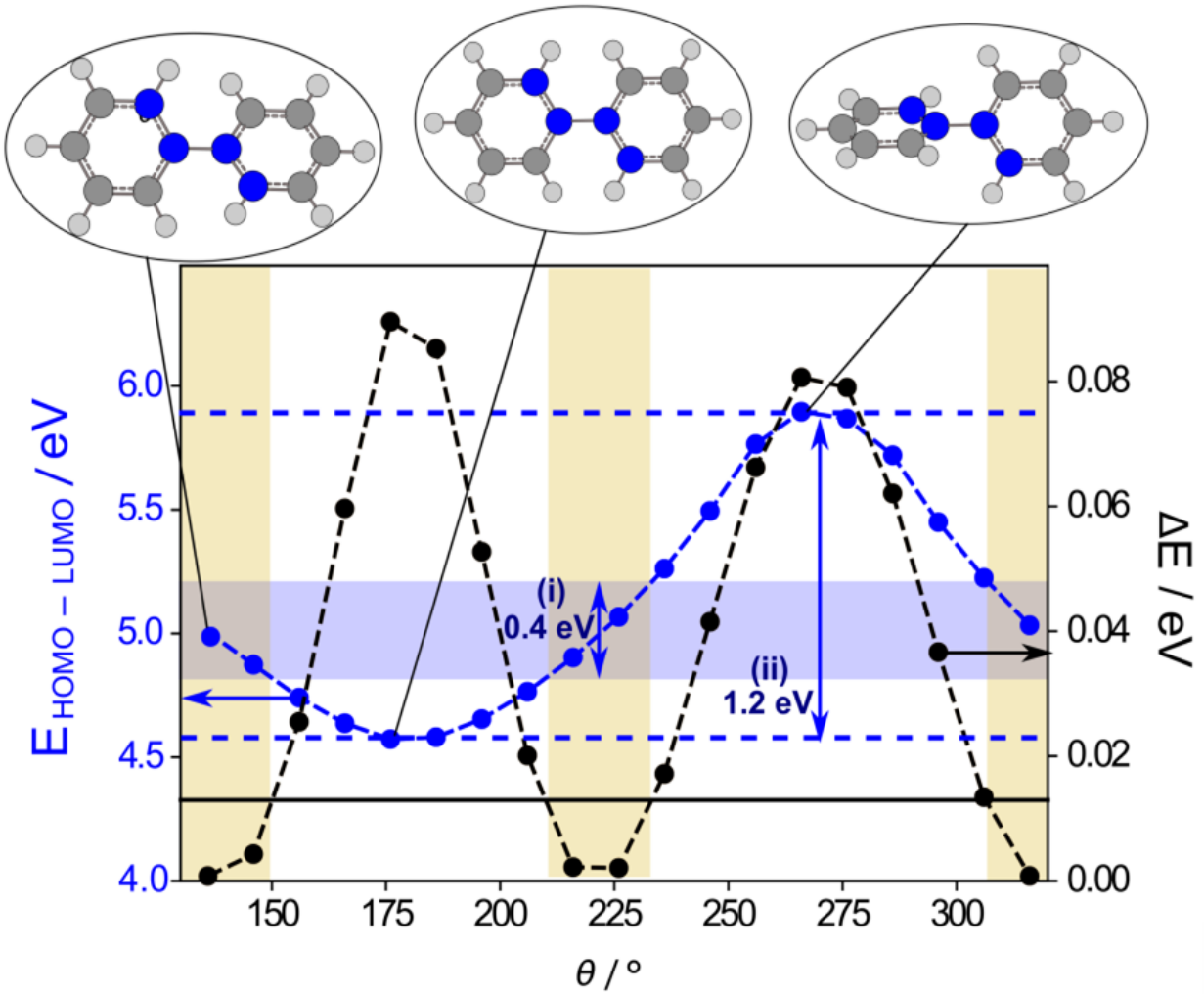


Cross-links have little impact on the band gap.



The largest fragment (lowest band gap) is most important.

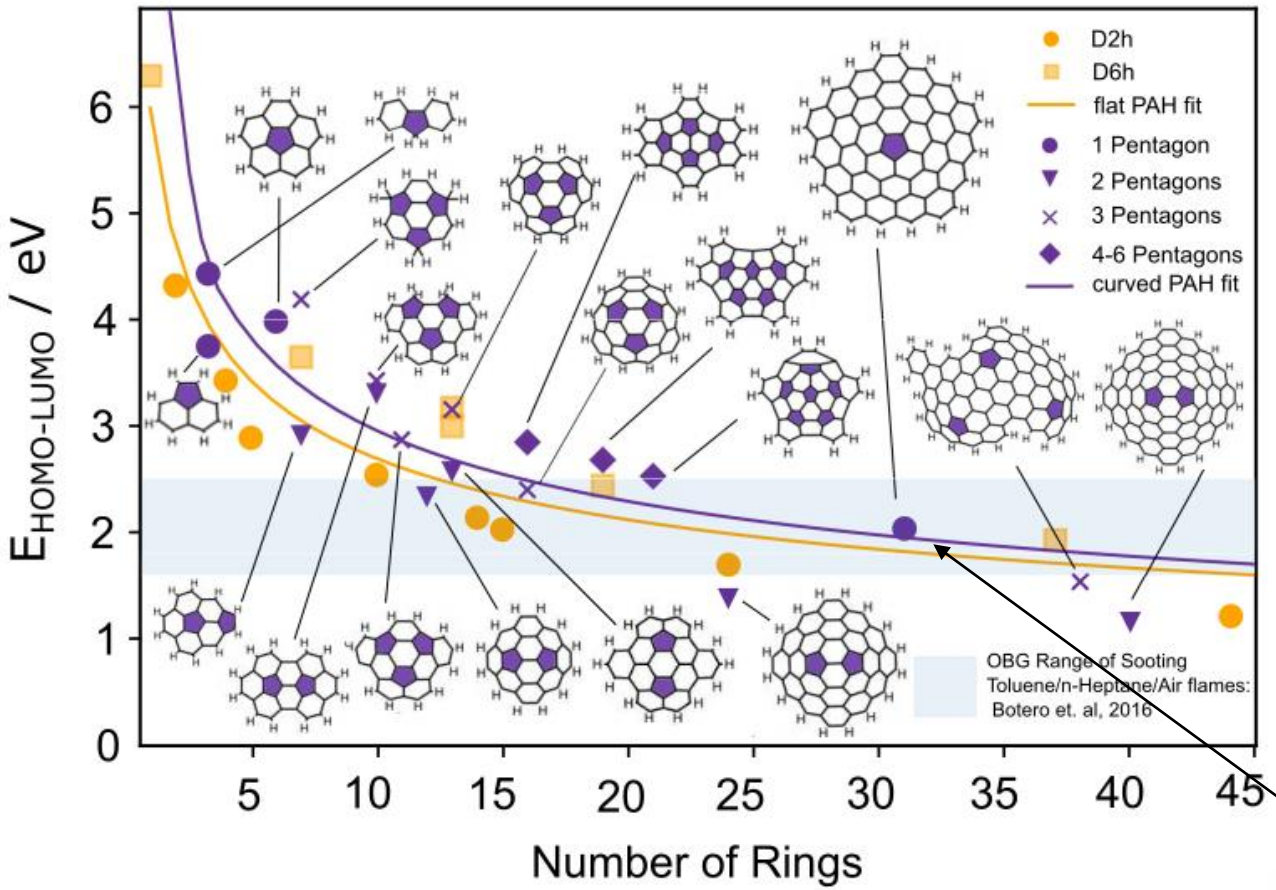
Effect of rotation on optical band gap



- Formation of cross-link enables rotation between fragments.
- Relaxed potential energy surface scan to check optical properties of different conformers and what energy is required.

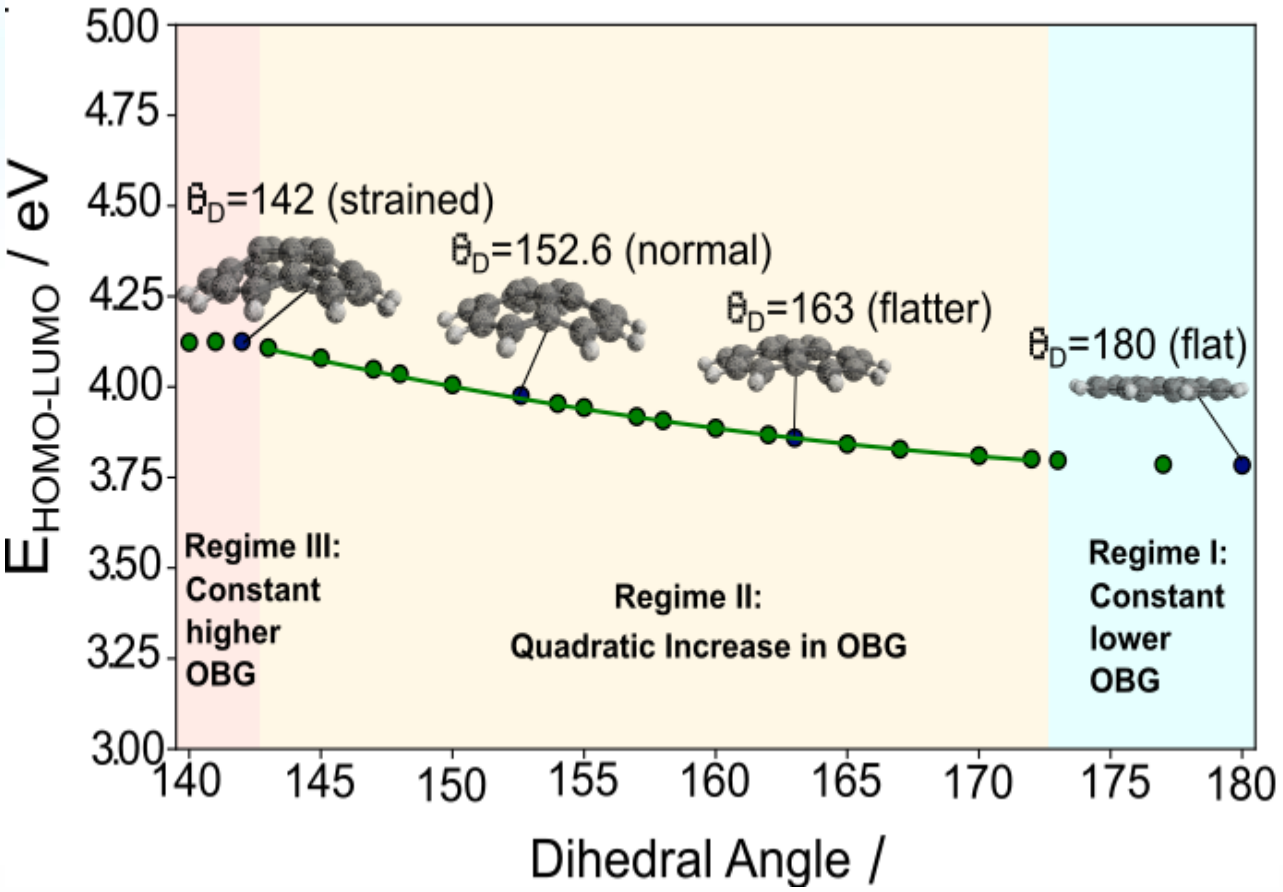
Rotation allows tunability of optical band gaps.

Curved vs. planar structures



- Curved structures also approach zero-band gap limit.
- More pentagons results in more curvature - higher optical band gap
- Curved nano-graphenes coincide with planar structures for larger sizes.

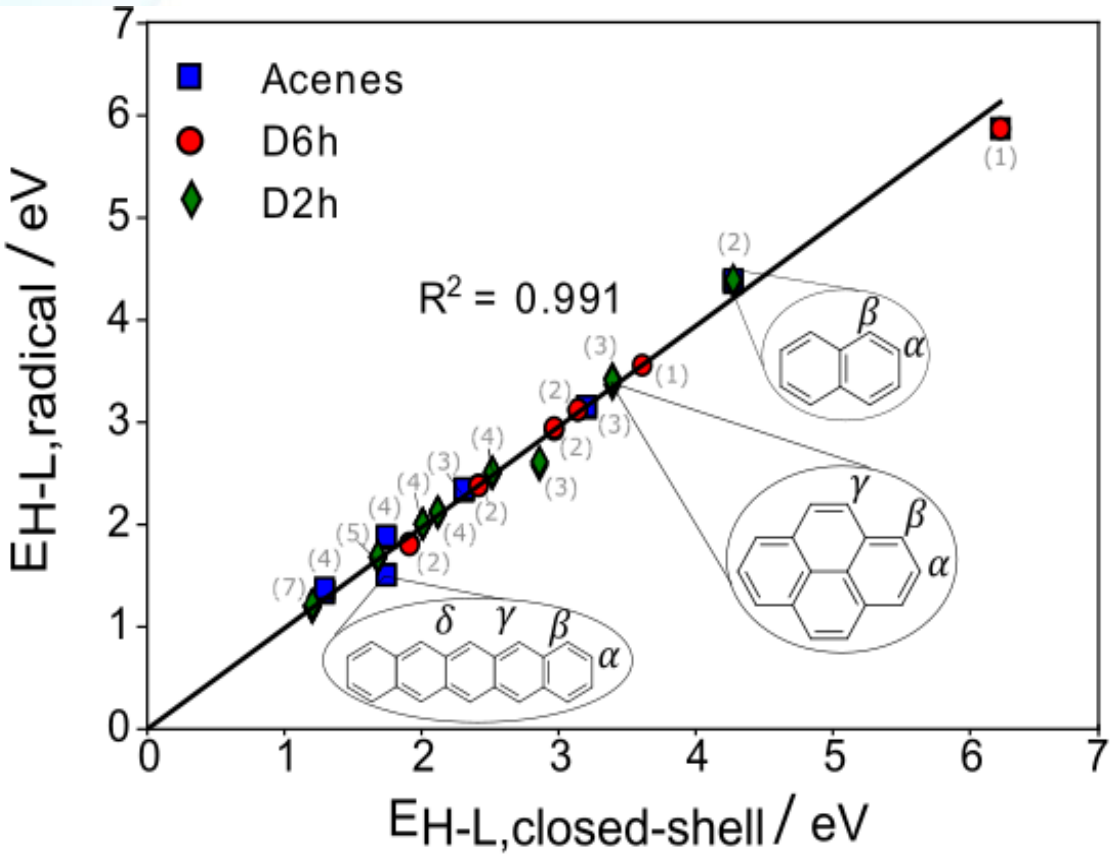
Rabenau, T., et al. Zeitschrift für Physik B Condensed Matter 90.1 (1993): 69-72.



- Curved structures also approach zero-band gap limit.
- More pentagons results in more curvature - higher optical band gap
- Curved nano-graphenes coincide with planar structures for larger sizes.

Smaller curved nano-graphenes have larger band gaps.

Radical vs planar structures

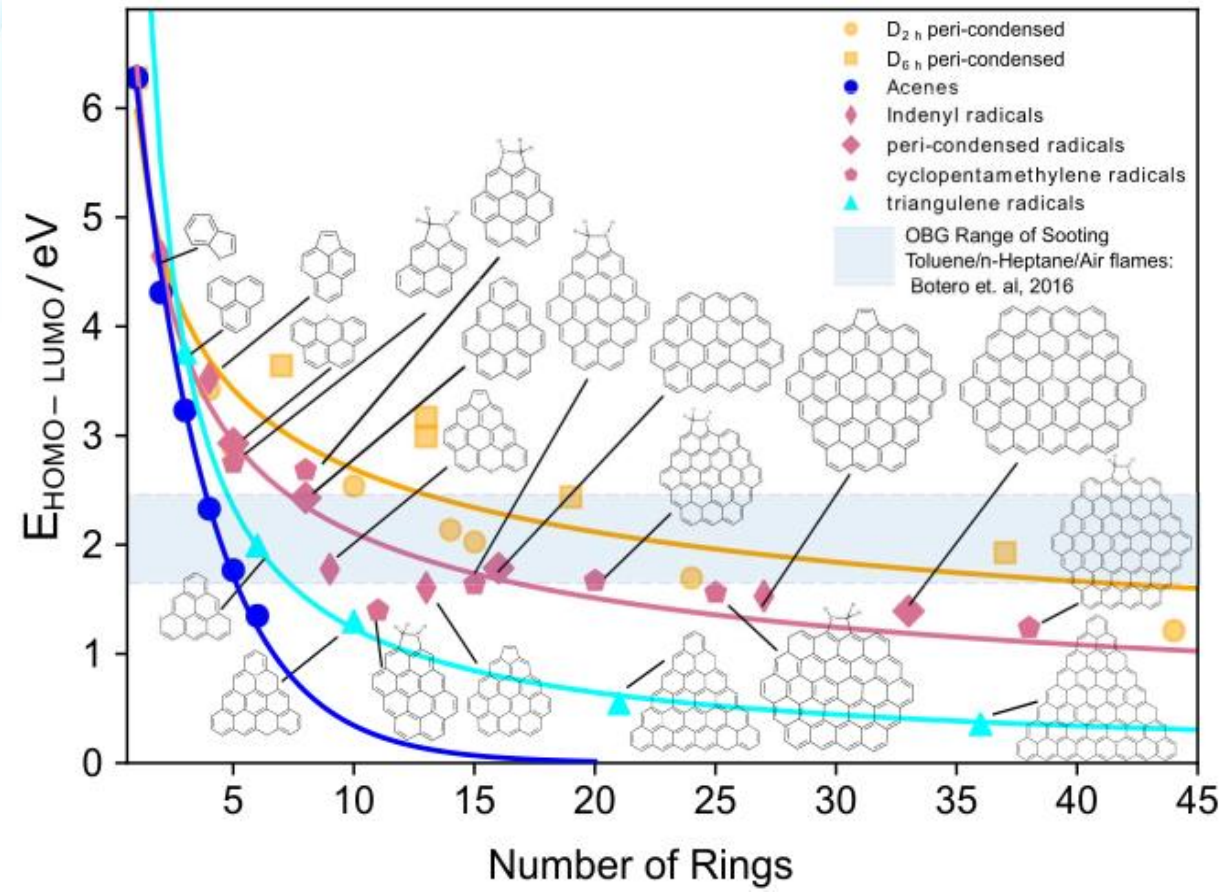


- A single σ-radical site does not affect the optical band gap.

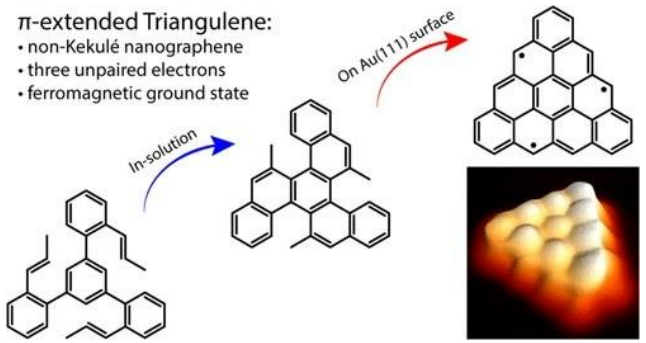
Hydrogen termination does not appear to influence band gap.

Mishra, Shantanu, et al. *Journal of the American Chemical Society* (2019).

Radical vs planar structures



- Delocalized radicals (odd carbon number) have significantly lower band gaps at all sizes.
- Multi-radical character reduces optical band gap as well.



Mishra, Shantanu, et al. *Journal of the American Chemical Society* (2019).

π-radical nanographenes have lower band gaps.

Conclusions

- The optical band gap of nano-graphenes is highly sensitive to the underlying structure – size, symmetry, curvature, and π-radical character are all important and could be useful for tailoring band gap to different applications.

- Other features are less impactful, with cross-linking and hydrogen termination not influencing the optical band gap significantly.

- OBGs observed in flames can be attributed to moderate sized model nano-graphenes, larger curved structures, or smaller π-radical structures.

PCCP

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Cite this: DOI: 10.1039/c9cp02363a

Optical band gap of cross-linked, curved, and radical polyaromatic hydrocarbons†

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Received 26th April 2019,
Accepted 27th June 2019

DOI: 10.1039/c9cp02363a

rsc.li/pccp

In this work, the optical band gaps of polycyclic aromatic hydrocarbons (PAHs) crosslinked *via* an aliphatic bond, curved *via* pentagon integration and with radical character were computed using density functional theory. A variety of different functionals were benchmarked against optical band gaps (OBGs) measured by ultraviolet-visible spectroscopy with HSE06 being most accurate with a percentage error of 6% for a moderate basis set. Pericondensed aromatics with different symmetries were calculated with this improved functional providing new scaling relationships for the OBG *versus* size. Further calculations showed crosslinks cause a small decrease in the OBG of the monomers which saturates after 3–4 crosslinks. Curvature in PAHs was shown to increase the optical band gap due to the resulting change in hybridisation of the system, but this increase saturated at larger sizes. The increase in OBG between a flat PAH and a strained curved one was shown to be equivalent to a difference of several rings in size for pericondensed aromatic systems. The effect of σ-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 formation.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrogen terminated graphene fragments ubiquitous in nature with a rich chemistry. A delocalised π-bonding network stabilises these pericondensed aromatics making them the thermodynamically preferred arrangement for hydrocarbons.[1] This stability makes them ubiquitous in thermal processes such as in interstellar dust,[2] the moon Titan's atmosphere[3,4] and terrestrial combustion.[5] Their rich chemistry has also attracted interest for molecular electronics with a variety of graphene ribbons synthesized and different schemes for tuning their electronic structure have integrating topological defects such as pentagonal rings are two such schemes for tuning the electronic properties that have not received much theoretical study to date. An example electronic application for PAHs curved by pentagon integration is their potential in batteries, as they have been shown to store large amounts of lithium.[7]

Our groups main interest is the role of PAHs as precursors for carbonaceous particulates in flames. A fundamental understanding of this process is of great interest, be it for mitigating emissions from combustion or for the commercial production of carbonaceous particles for applications such as tire filler materials, dyes, paints, and molecular electronics.[8] Such an

Thank you for listening

Johnson Matthey

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This project is funded by the
National Research Foundation (NRF),
Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme.

State	Literature Method	Literature Vertical Excitation Energy / eV	This work / eV
Pyrene - 2nd bright state	MRCI	3.81	3.73
Circumpyrene - 1st excited singlet state	MRCI	2.22	2.41
Circumpyrene - 2nd excited singlet state	MRCI	2.36	2.54
Circumcoronene - 1st excited singlet state	MRCI	1.94	2.15
Circumcoronene - 2nd excited singlet state	MRCI	2.37	2.39
Phenalenyl – 1st excited state	RAS-CI	2.76	2.82
Phenalenyl – 2nd excited state	RAS-CI	3.04	3.05
Triangulene – Singlet excited state	RAS-CI	0.57	0.52
Triangulene – Triplet excited state	RAS-CI	2.82	2.71
10-ring Triangulene – Quartet excited state	CASSCF	3.3	2.8
10-ring Triangulene – Quartet excited state	MR-CISD	3.1	
10-ring Triangulene – Quartet excited state	MR-CISD+Q	3.0	

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