



# Penta-ring crosslinking in nascent soot formation

## INTRODUCTION

- The least understood stage of particulate formation in combustion processes is the inception of gas phase aromatics to condensed clusters.
- Molecular dynamics studies have shown that the binding energy between medium-sized PAHs is not strong enough to stabilize the dimer or trimer and avoid evaporation at high temperatures [1].
- Recent mass spectrometry with tunable photoionization using synchrotron radiation experiments have identified that many of the early aromatics found in flames contain pentagonal rings around their perimeter [2].
- In a recent paper, high-resolution atomic force microscopy was used for direct imaging of the building-blocks forming the particles in the early stages of soot formation. The detected aromatic compounds include molecules with a significant presence of penta-rings and also large compounds composed of two aromatic molecules connected with a double bond between penta-rings [3].

A NEW CROSSLINKING REACTION BETWEEN PENTAGONAL RINGS AROUND THE PERIPHERY OF PLANAR PERICONDENSED AROMATIC MOLECULES IS EXPLORED FOR NASCENT SOOT FORMATION.

## METHODS

### 1. DENSITY FUNCTIONAL THEORY CALCULATIONS

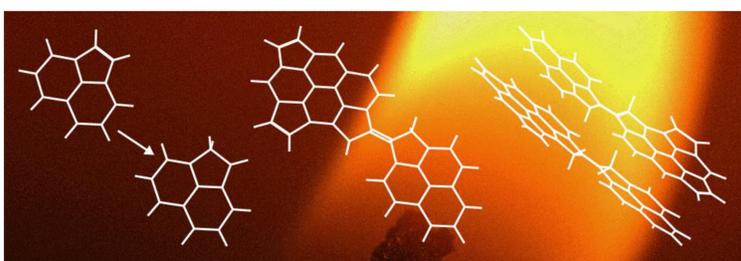
- Geometry optimisations to determine minimum energy and transition states.
- Frequency calculations to ensure transition states have a single imaginary frequency. (Gaussian 09, M06-2X/6-311g(d,p) // B3LYP/6-311+g(d,p))

### 2. WELL-TEMPERED METADYNAMICS SIMULATIONS

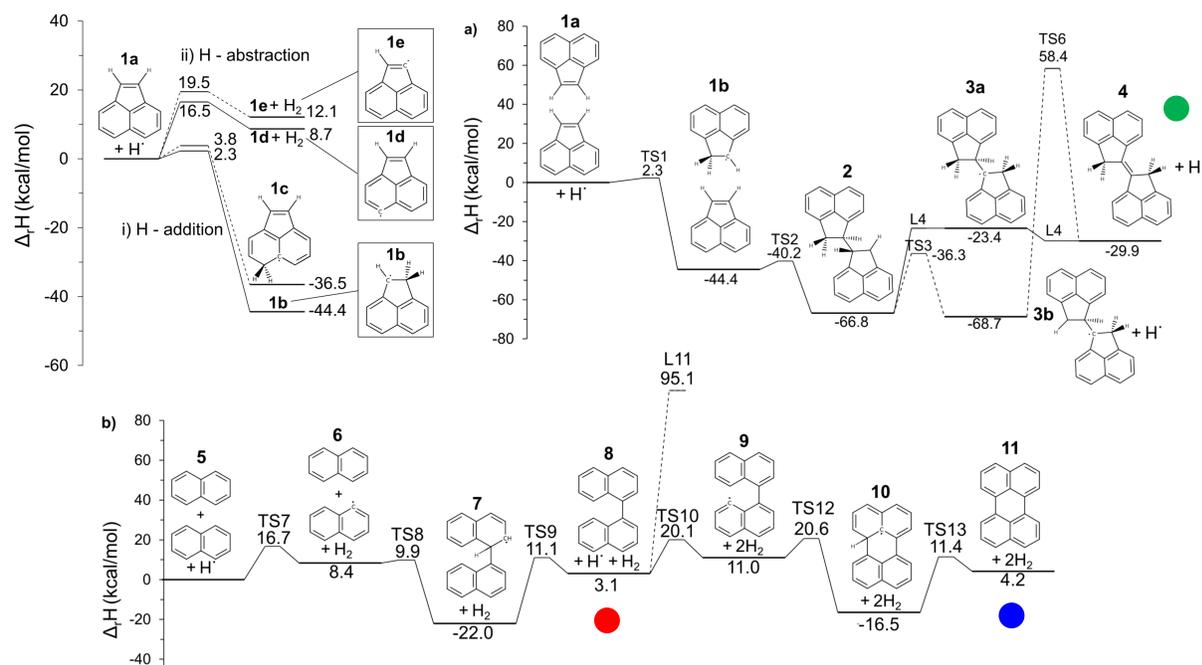
- Free energy (FE) profiles of physical dimerization of PAHs.

### 3. MOLECULAR DYNAMICS SIMULATIONS

- Dynamic behaviour (percentage of clustered molecules, number of clusters, cluster sizes, cluster lifetimes).



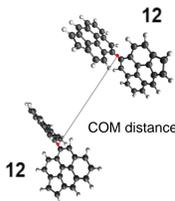
## REACTION PATHWAYS



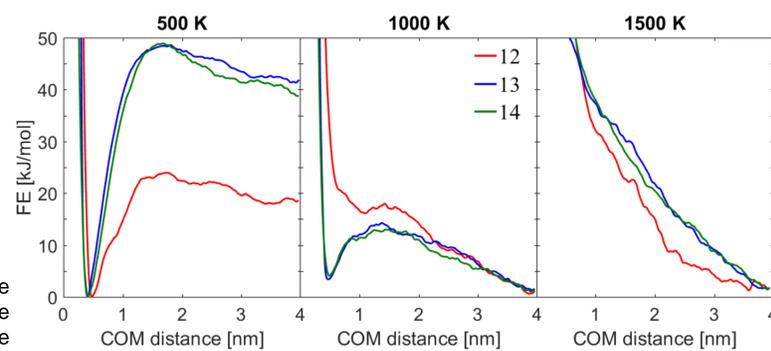
## NUCLEATING BEHAVIOUR

### FREE ENERGY PROFILES

The distance between the center of masses of the two monomers (COM) has been selected as collective variable.



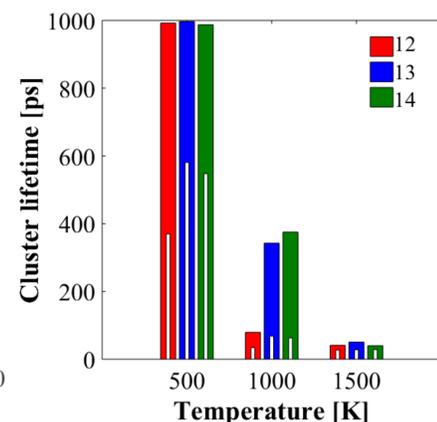
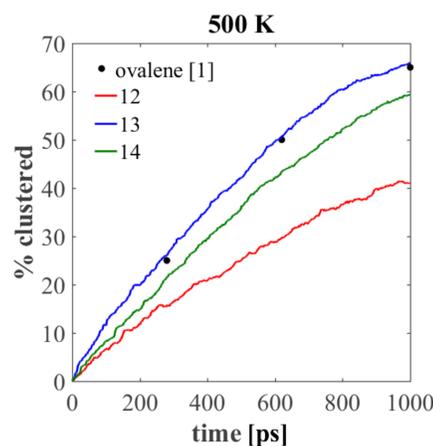
The dimerization propensity is defined as the FE difference ( $\Delta FE$ ) between the dimer-state (minimum of the FE) and the monomer-state (FE calculated at long distances).



Species	$\Delta FE$		
	500 K	1000 K	1500 K
11	-18	15	-
12	-42	4	-
13	-40	4	-

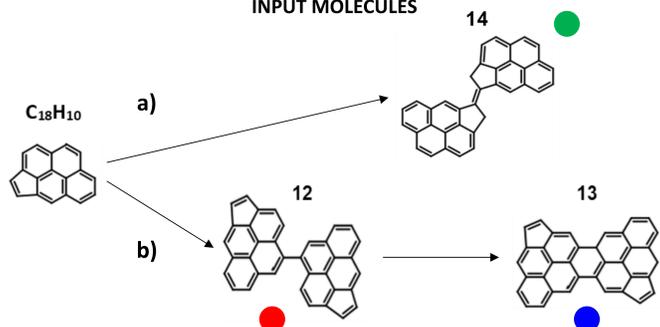
### MD RESULTS

- The presence of the double bond gives planarity to the structure making species 13 and 14 very similar.
- The presence of aliphatic bond in 12 destabilizes the dimer and cluster formation.



PARAMETERS	WT-META	MD
Software	GROMACS+PLUMED	GROMACS
Integrator	Langevin	Velocity Verlet
$\Delta t$	1 fs	
Ensemble, thermostat	NVT, Langevin	NVT, Nose-Hoover chains
T	500 K, 1000 K, 1500 K	
Force field	Intermolecular forces: opls-aa Intramolecular forces: iso-PAHAP	
Trajectories	3 x 100 ns	5 x 1 ns
Other parameters	Gaussian-shaped bias (height of 0.5 kJ/mol, width of 0.04 nm, deposited every 100 fs, bias factor 10 kJ/mol)	500 molecules, $1 \times 10^{18}$ PAHs/cm <sup>3</sup> , cluster definition ( $r_{crit}=1.5$ nm, $t_{crit}=20$ ps)

### INPUT MOLECULES



## CONCLUSIONS

- Hydrogen addition is found to be favourable on the electron-rich double bond region of a pentagonal ring.
- Crosslinking with another pentagonal ring rapidly forms and slowly expels hydrogen to become planar with a double bond holding the two PAHs together.
- Molecular dynamics and metadynamics suggest such a fragment clusters as effectively as a pericondensed species of the same size.

## REFERENCES

- Totton et al., Phys. Chem. Chem. Phys., 2012, 14, 4081-4094.
- Johansson et al., J. Phys. Chem. A, 2017, 121, 4475-4485.
- Schulz et al. Proc. Combust. Inst., 2018, in press.

This poster presents work from the CAPRICORN work packages.

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

Laura Pascasio<sup>a</sup>, Dingyu Hou<sup>b</sup>, Angiras Menon<sup>a</sup>, Jacob W. Martin<sup>a</sup>, Xiaoqing You<sup>b</sup> and Markus Kraft<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge

<sup>b</sup> Center for Combustion Energy, Tsinghua University

Contact lp521@cam.ac.uk, mk306@cam.ac.uk

