# *Ab initio* study of the dependence of the reactivity upon carbon nanotube diameter

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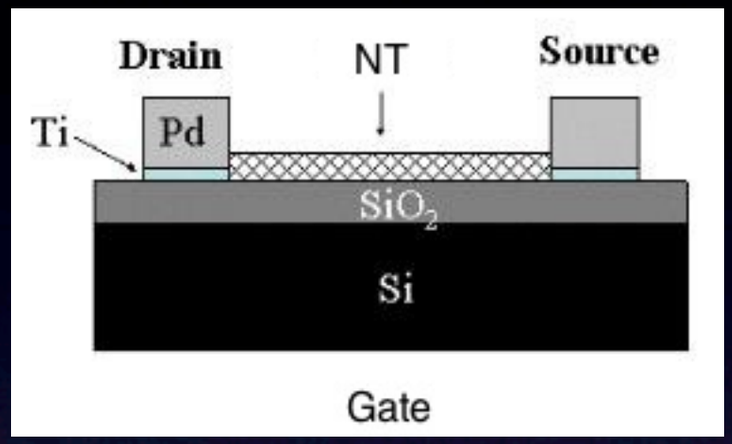
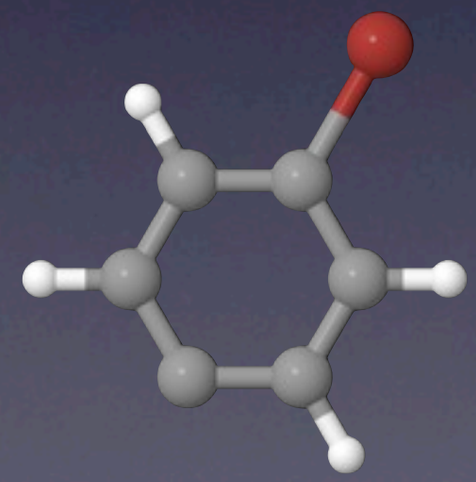
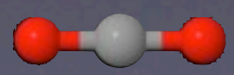
# Motivation

- NTs application : faster FETs




- Select NT by :
  - metallicity / semiconductivity
  - diameter
- Potential purification methods studied :
  - bromo-phenyl functionalization
  - combustion by $CO_2$





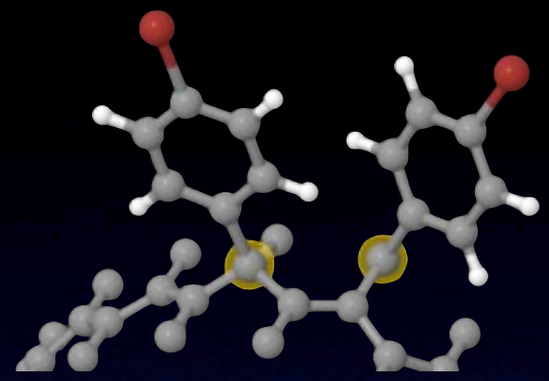
# Method

- Density Functional Theory (DFT)
  as implemented in Abinit [1] and ONETEP[2]
  - Abinit : plane wave basis
    - very tight and controllable convergence
    - small (~100 atoms) systems
  - ONETEP : nonorthogonal generalized Wannier functions basis
    - large (~100 000) systems
    - harder to control convergence
- zigzag (n,0) NTs :
  - small primitive cell (low computational cost)
  - can be metallic or semiconducting
- Local Density Approximation (LDA)
- Forces fully relaxed

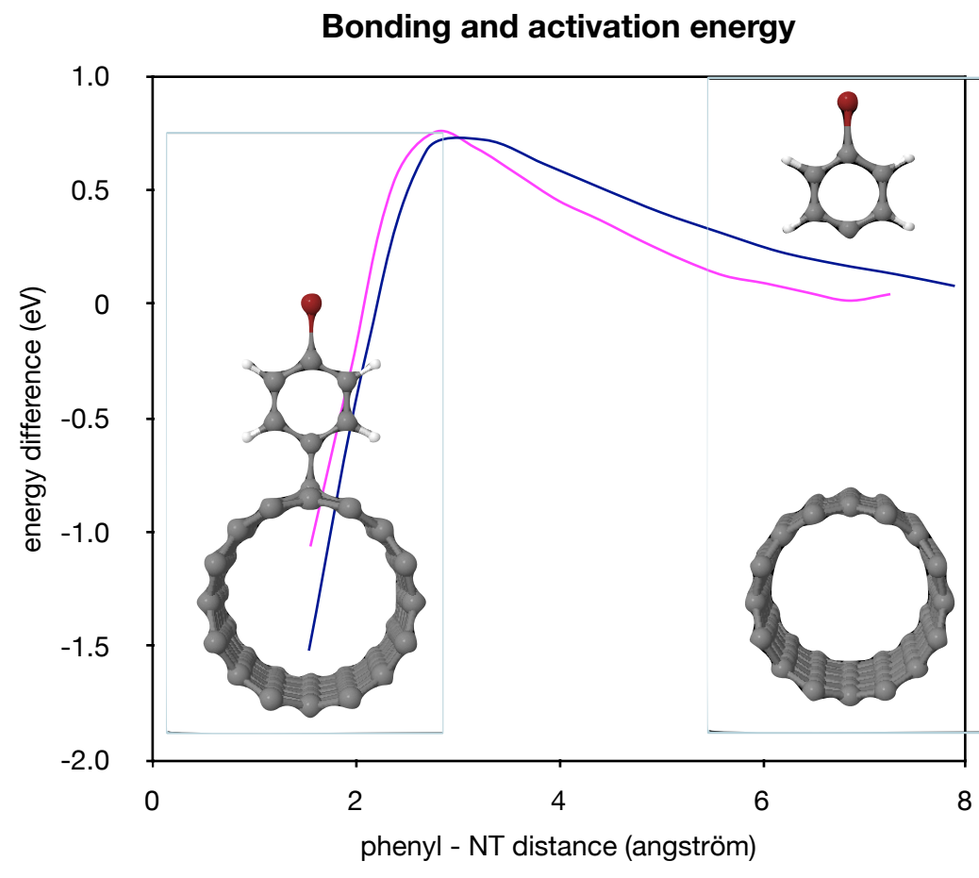
[1] : Gonze et al. , Computer Phys. Commun. **180**, 2582-2615 (2009).
[2] : Skylaris, Haynes, Mostofi and Payne, J. Chem. Phys. **122**, 084119 (2005)

# Bromo-phenyl functionalization

- hypothesis :
  - limiting process :
    binding of the first phenyl to the NT [3]
  - reaction path :
    linear extrapolation between 2 states



- What we want to know :
  activation energy (thermodynamics) (costly)
- Easier way :
  1) bonding energy :
  - opposite trend wrt activation
  - cheaper
  2) activation energy calculation (min. set)




[3] : Margine, Bocquet, Blase, Nano Letters **8**, 3315-3319 (2008)

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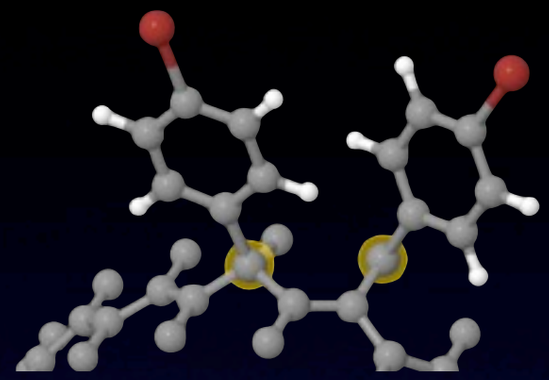

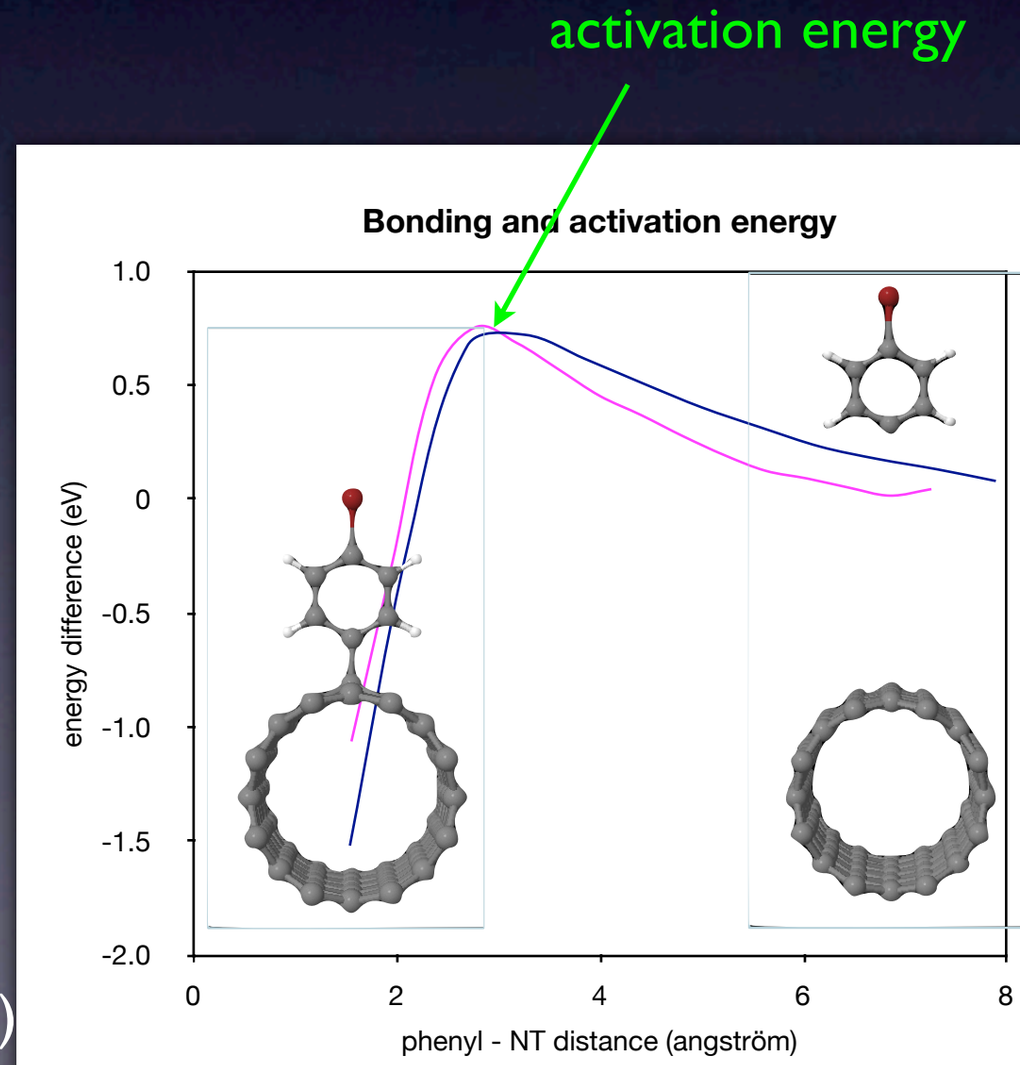


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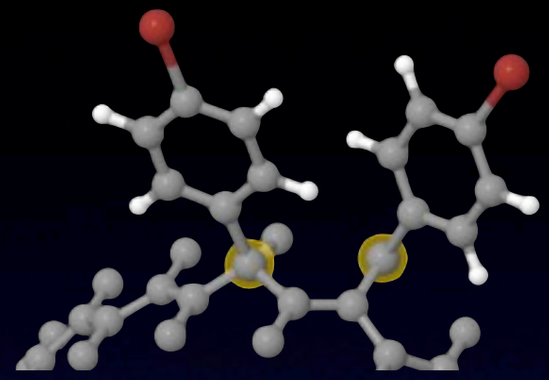

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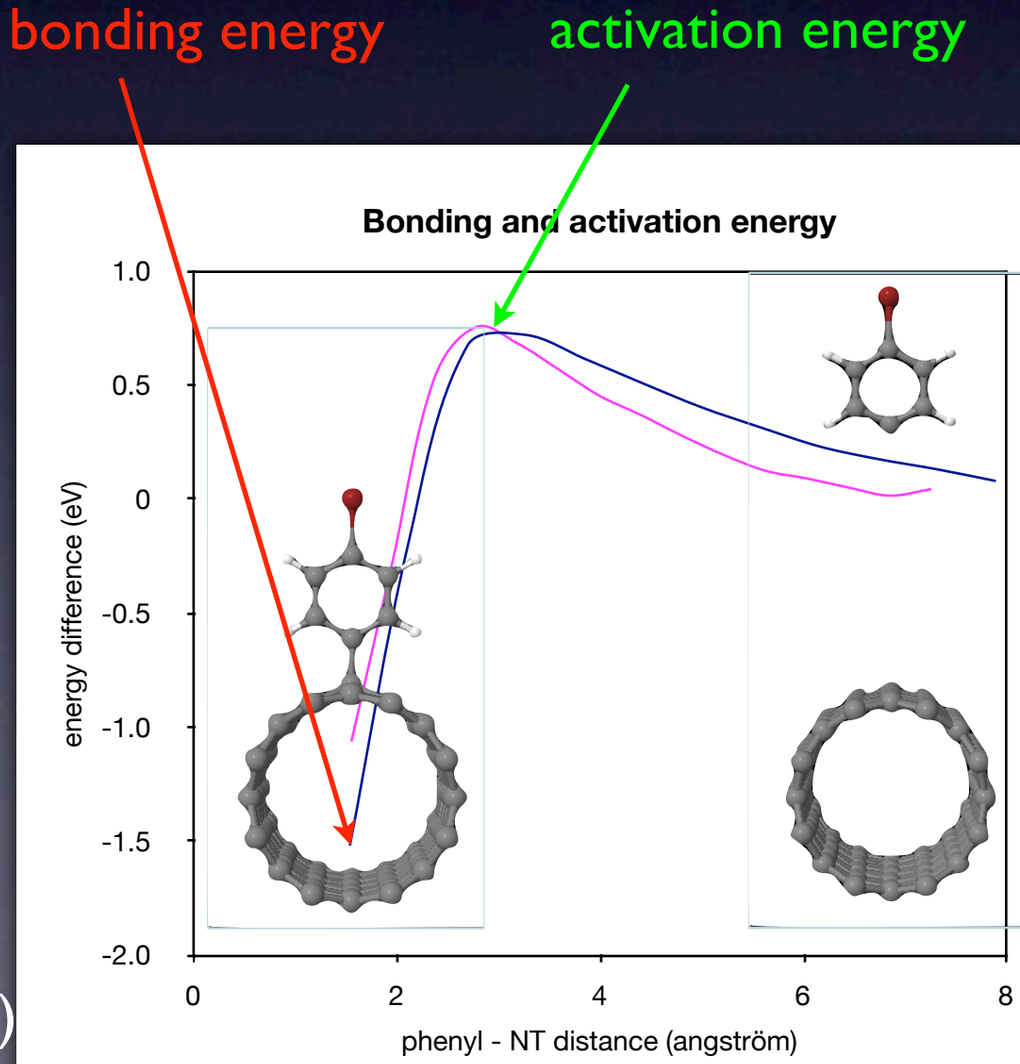


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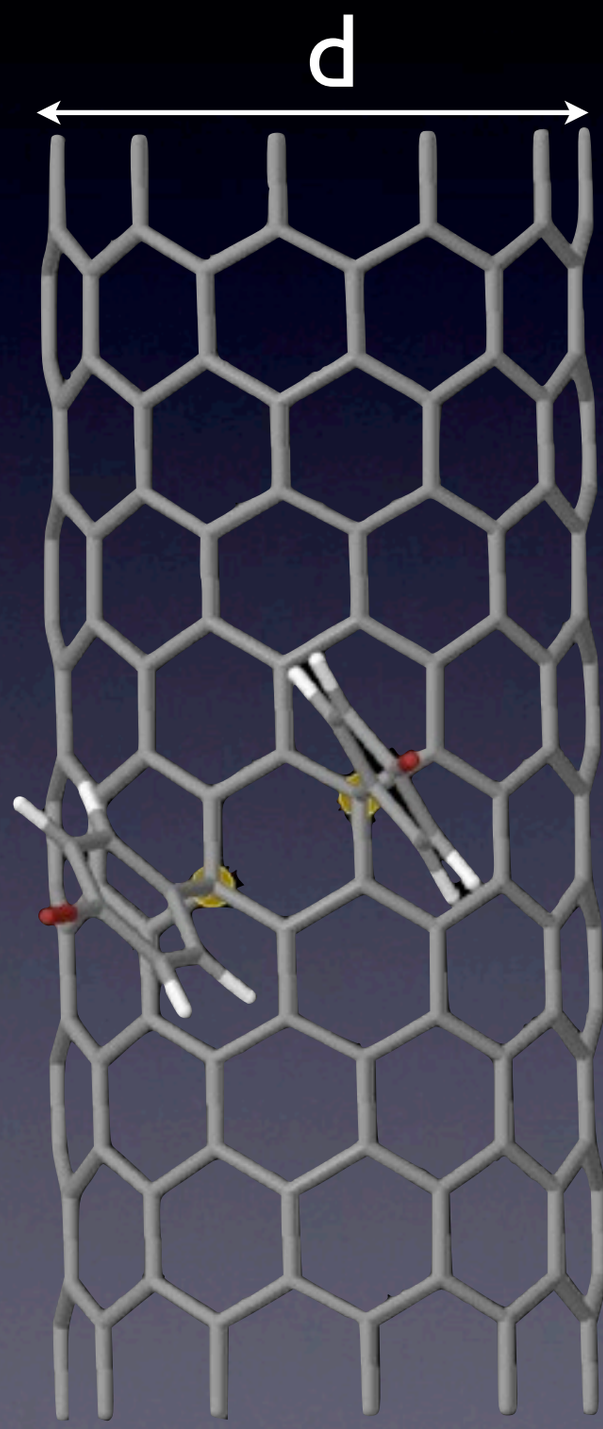
# Bromo-phenyl bonding energy

- Configuration :
  - para
    (the most stable [3])
  - Isolated pairs
    (1 per 5 primitive cells)
- Bonding energy (ΔE) with respect to
  - tube diameter (d)
  - metallicity or semiconductivity

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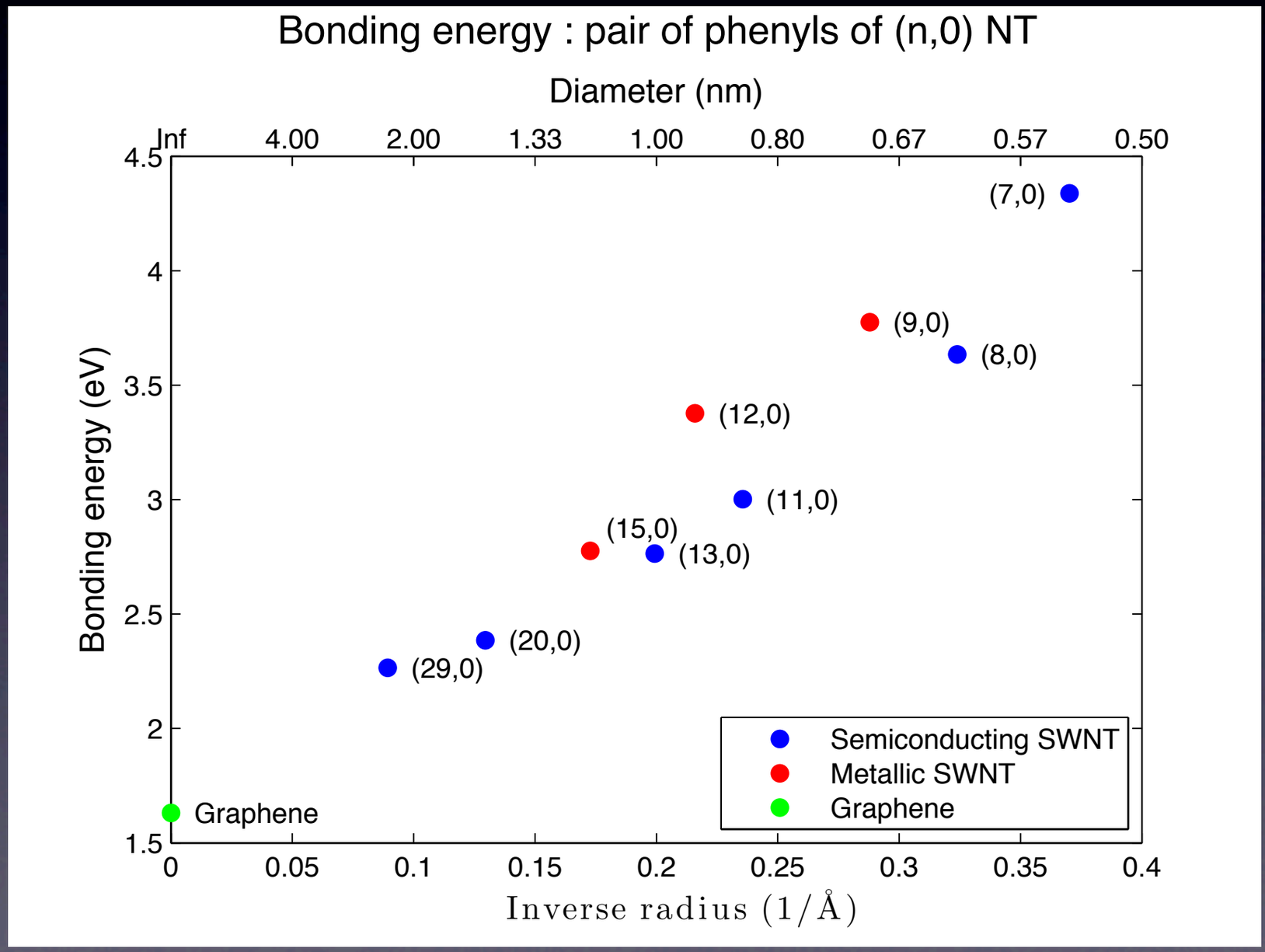
# Bonding energy

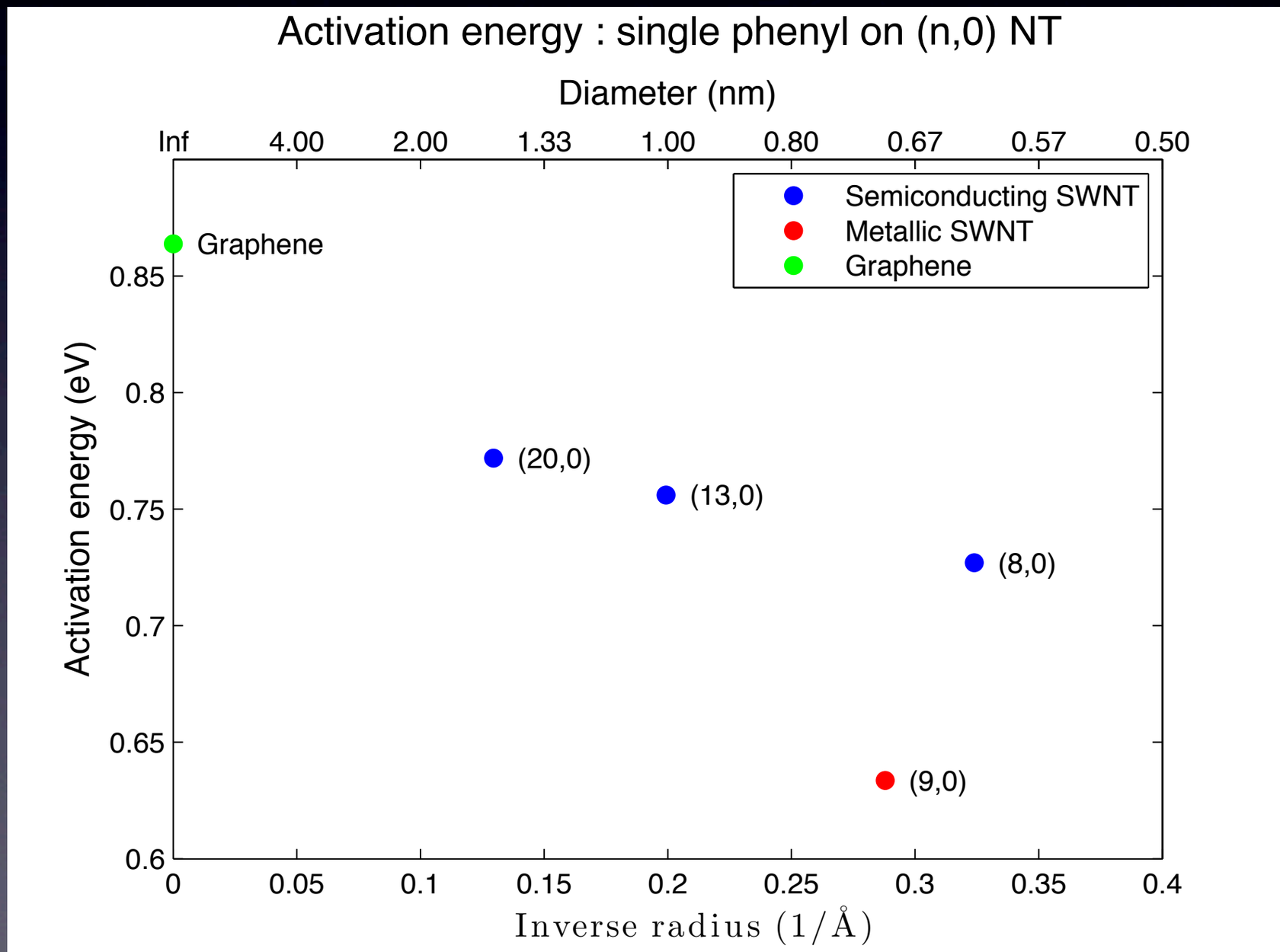
- Trend :
  - Bonding energy ↗ for smaller NTs
  - Bonding energy ↗ for metallic NTs
- We expect functionalization ↗ :
  - for smaller NTs
  - for metallic NTs



# Activation energy trend

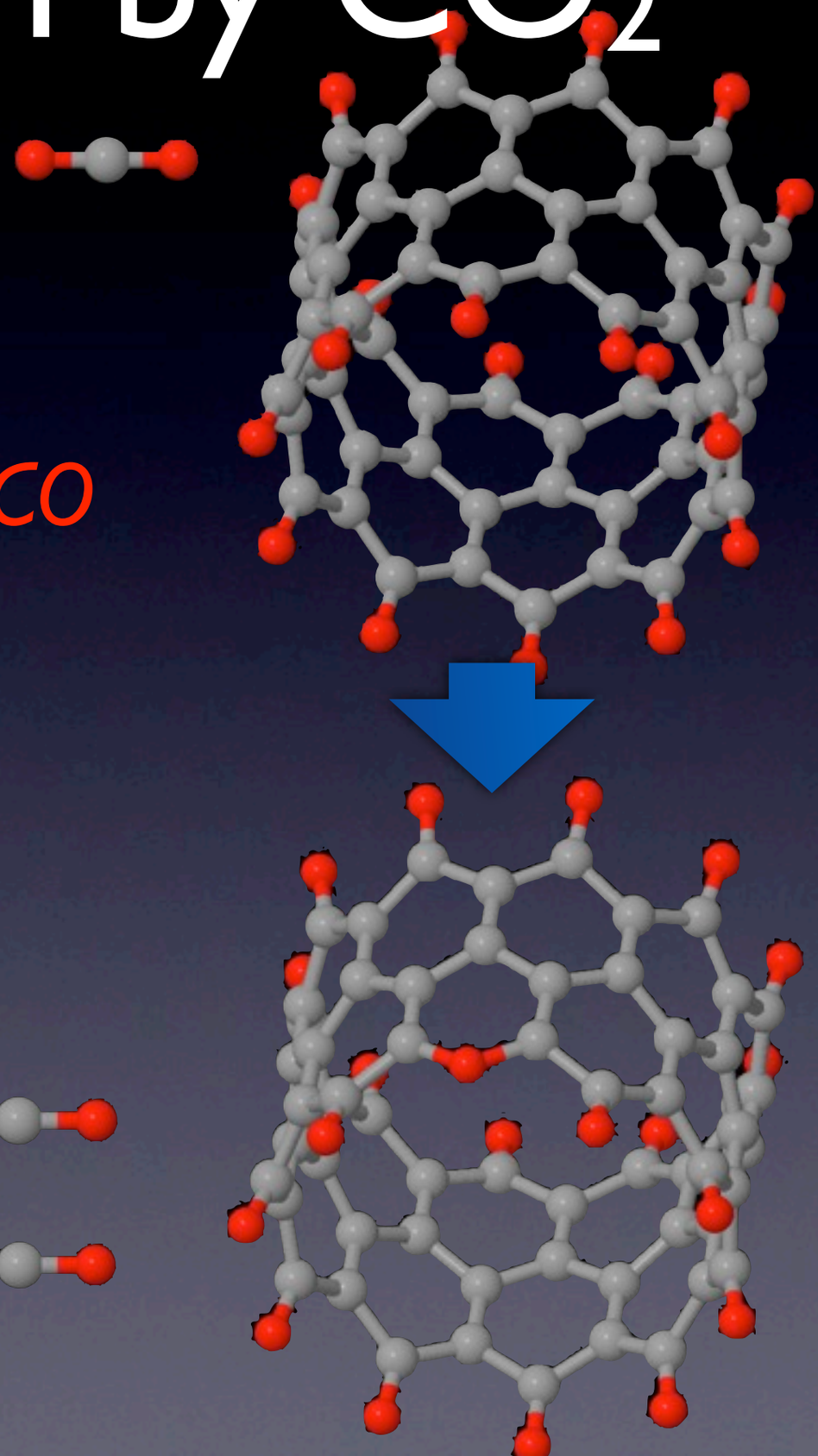
Trends :

- activation energy ↘
  - for smaller NTs
  - for metallic NTs
- confirm : functionalization ↗
  - for smaller NTs
  - for metallic NTs



# NT combustion by $CO_2$

- 2nd purification mechanism :
  NT combustion by $CO_2$
  *$NT + CO_2 + \Delta E \rightarrow (NT - C) + 2\ CO$*
- Model :
  - Finite NT (oxygen terminated)
  - edge carbon attacked
- Study :
  $\Delta E$ vs diameter
  for semiconducting NTs



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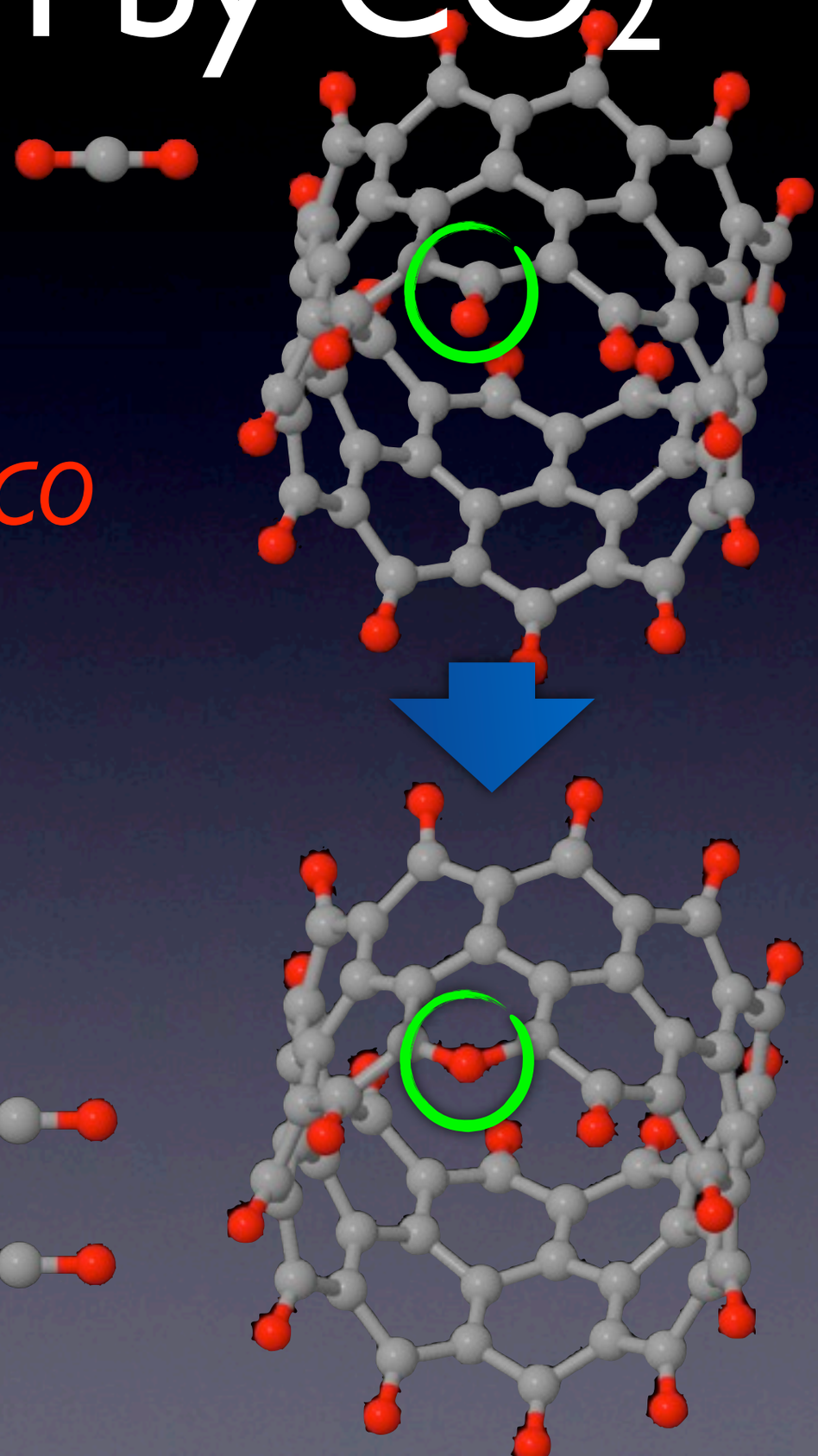
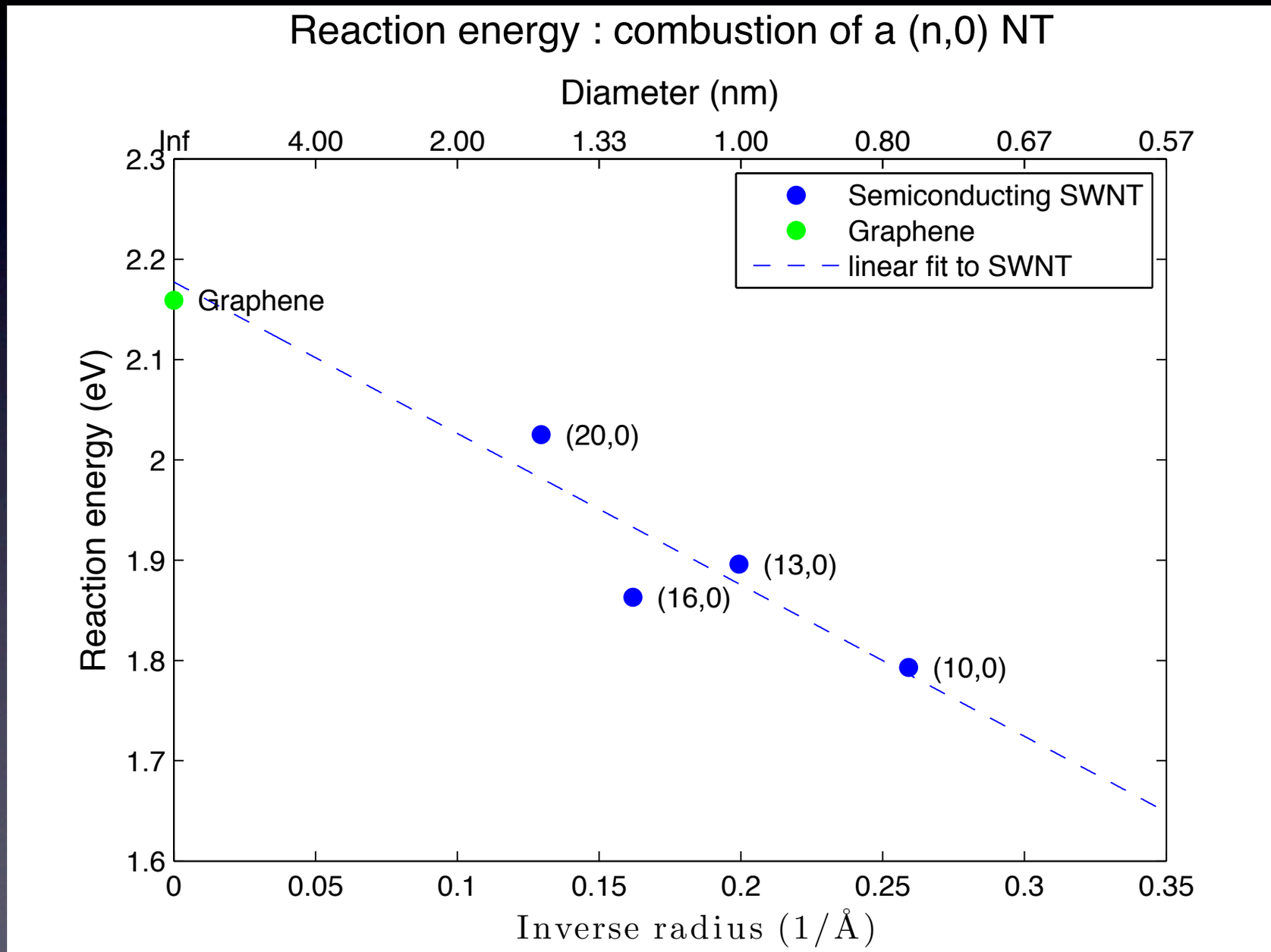


# NT combustion by $CO_2$

- Trend :
  faster combustion
  for smaller NTs
- Use :
  select larger NTs
  (opposite to phenyl)



# Conclusion

- Bromo-phenyl functionalization selects (solubilizes most) :
  - small NTs
  - metallic NTs
- Combustion by CO2 selects (leaves most intact) :
  - large NTs