Tunneling Current Increasing with Barrier Width explained using a 2-barrier Model

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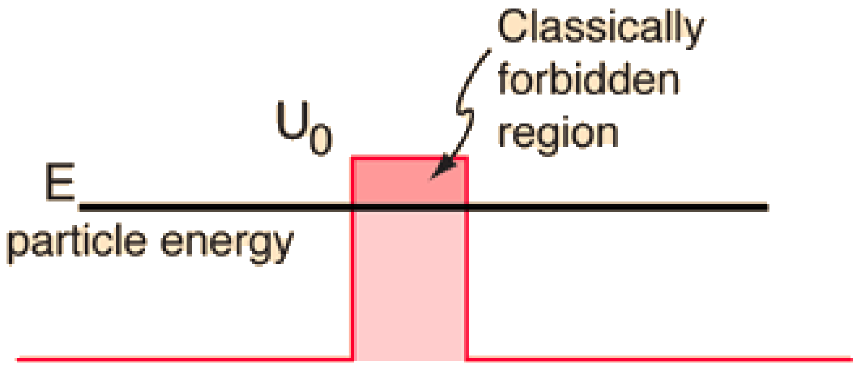
Stratingh Institute for Chemistry
University of Groningen, The Netherlands

We all learnt in kindergarten…

Tunnelling through a rectangular barrier…



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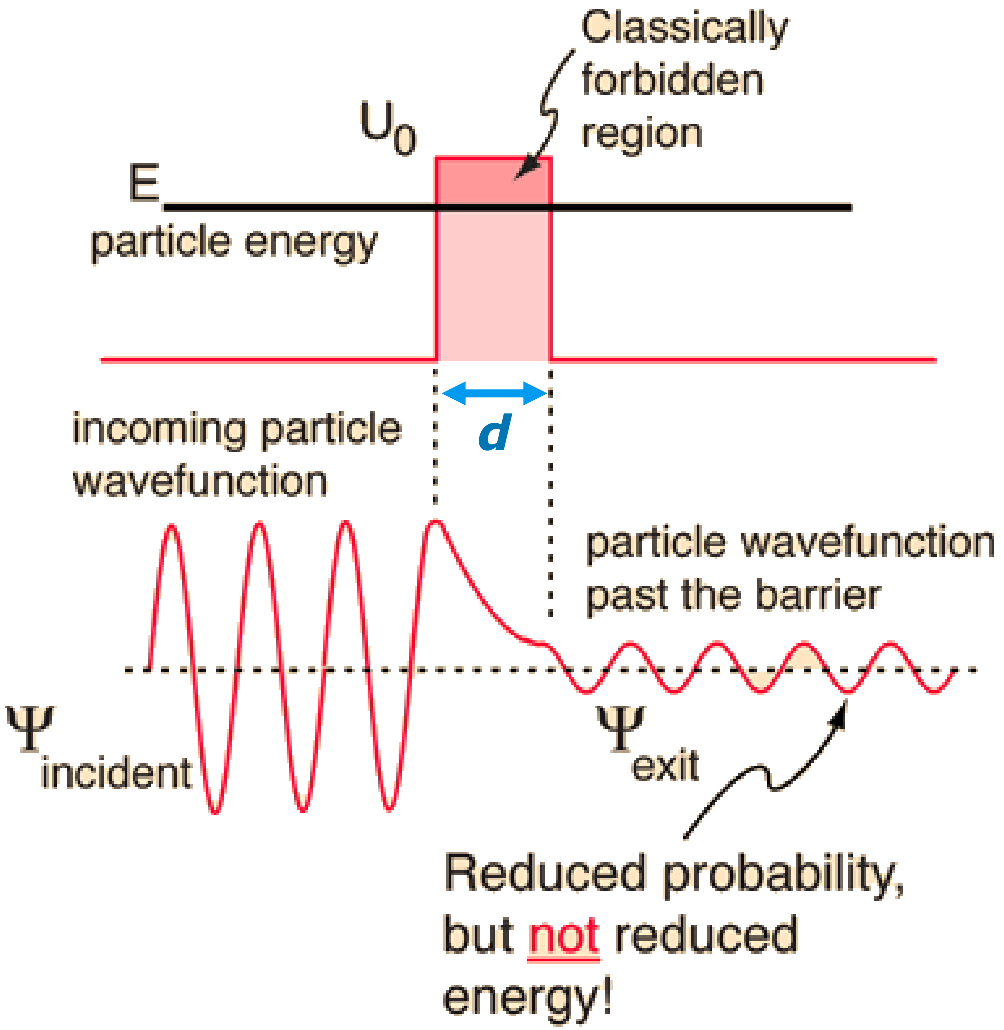

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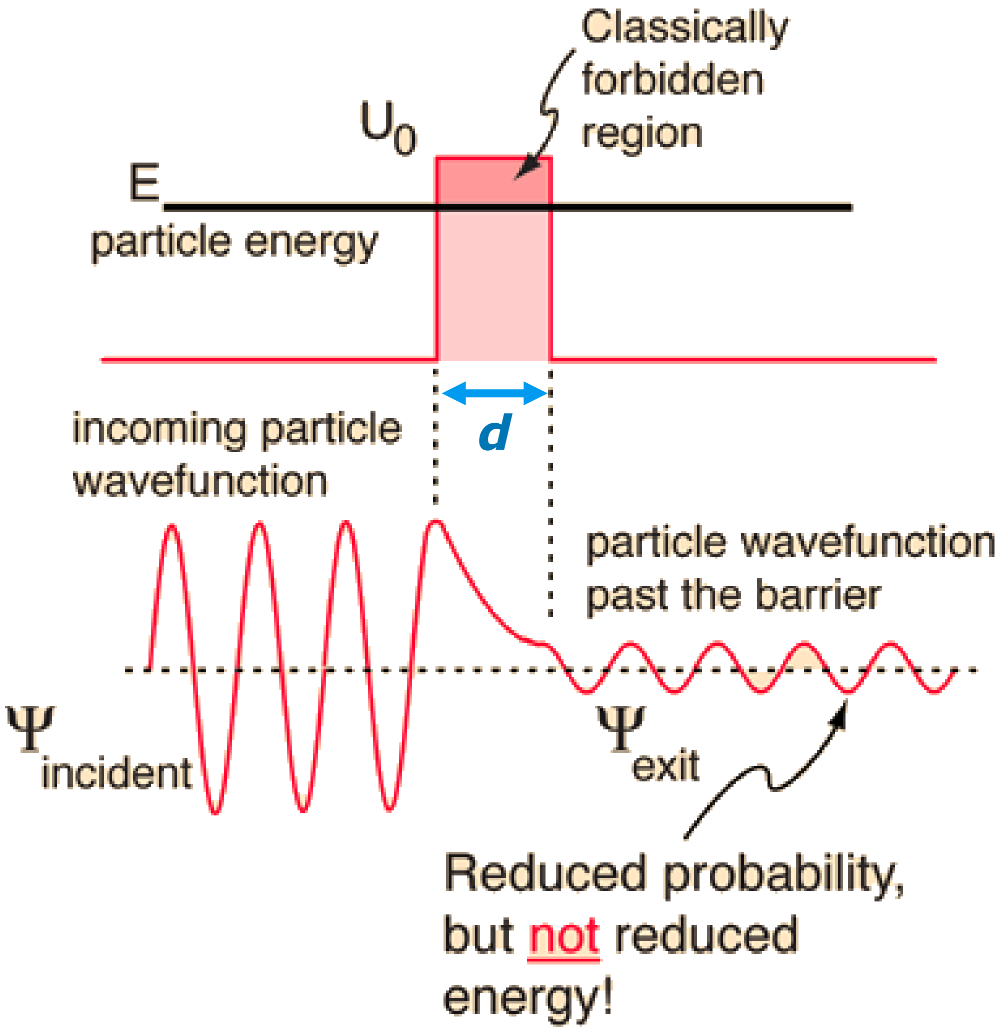
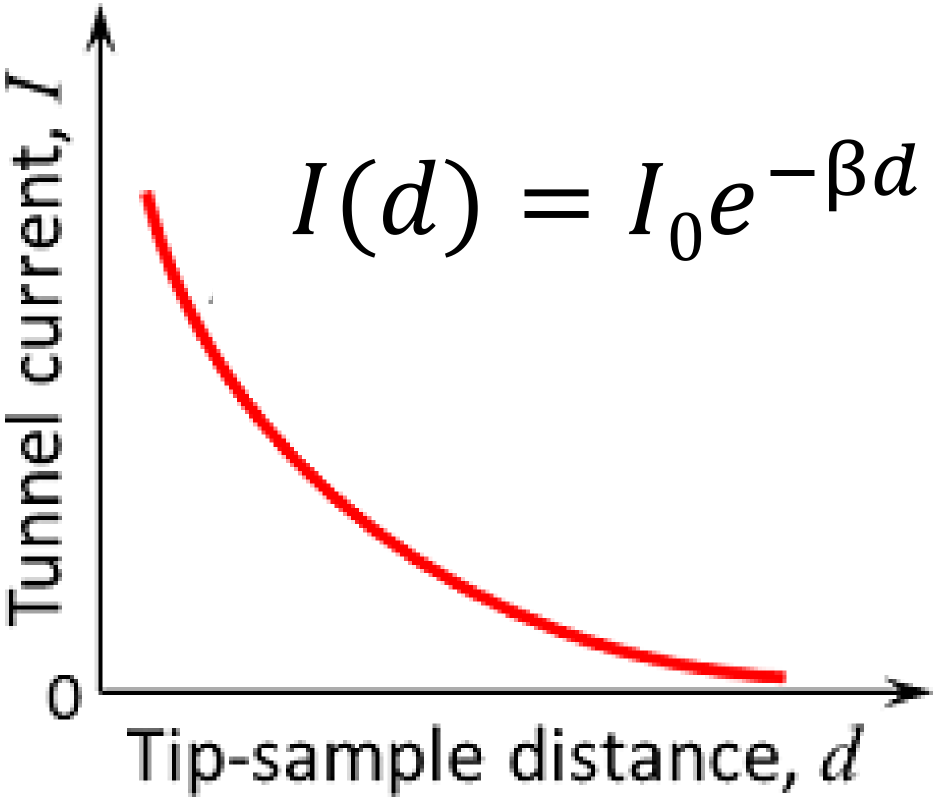
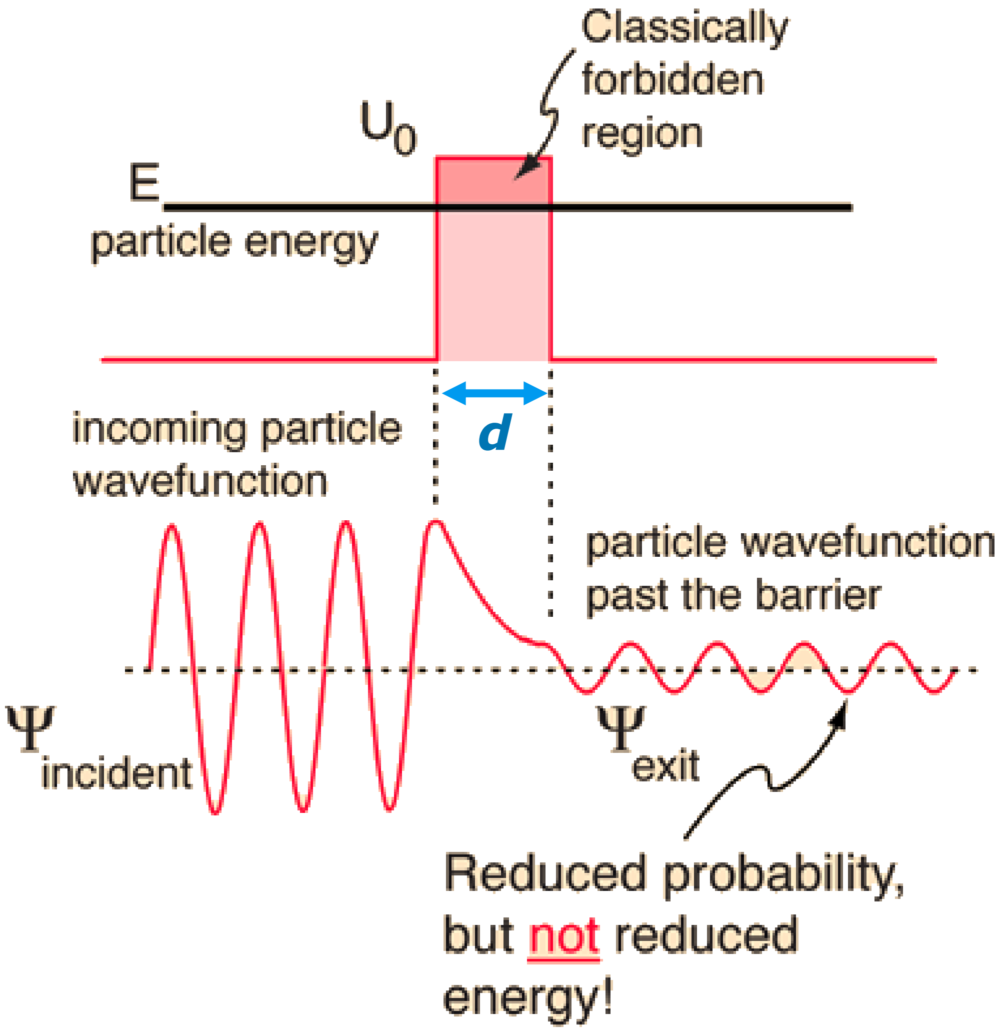




$$I(d) = I_0 e^{-\beta d}$$

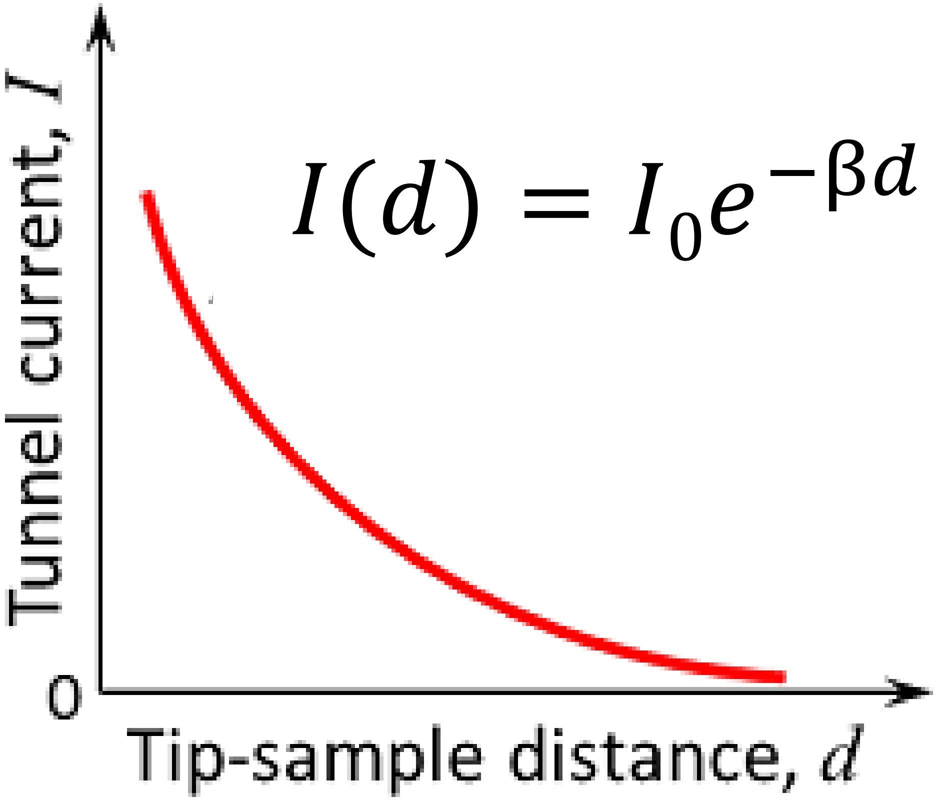
We all learnt in kindergarten…

Tunnelling through a rectangular barrier…



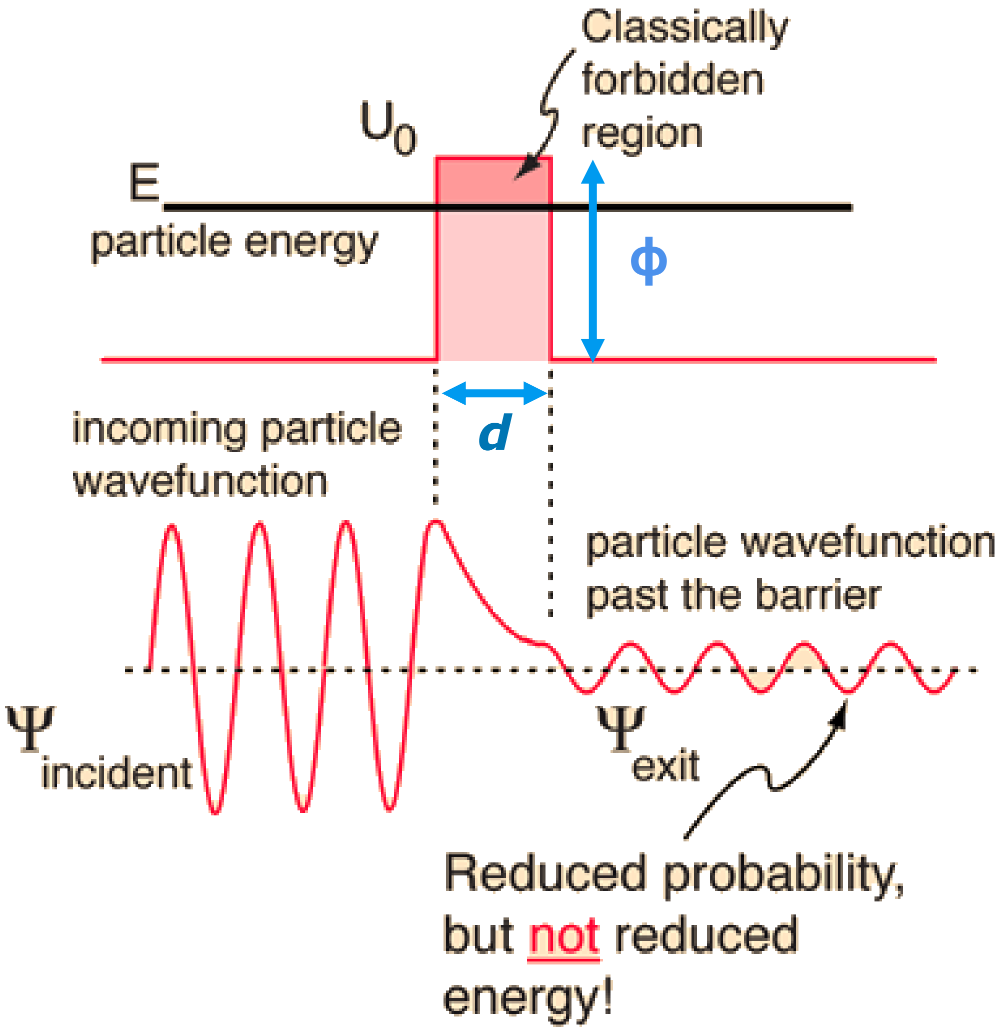
β = constant

$$I(d) = I_0 e^{-\beta d}$$



We all learnt in kindergarten…

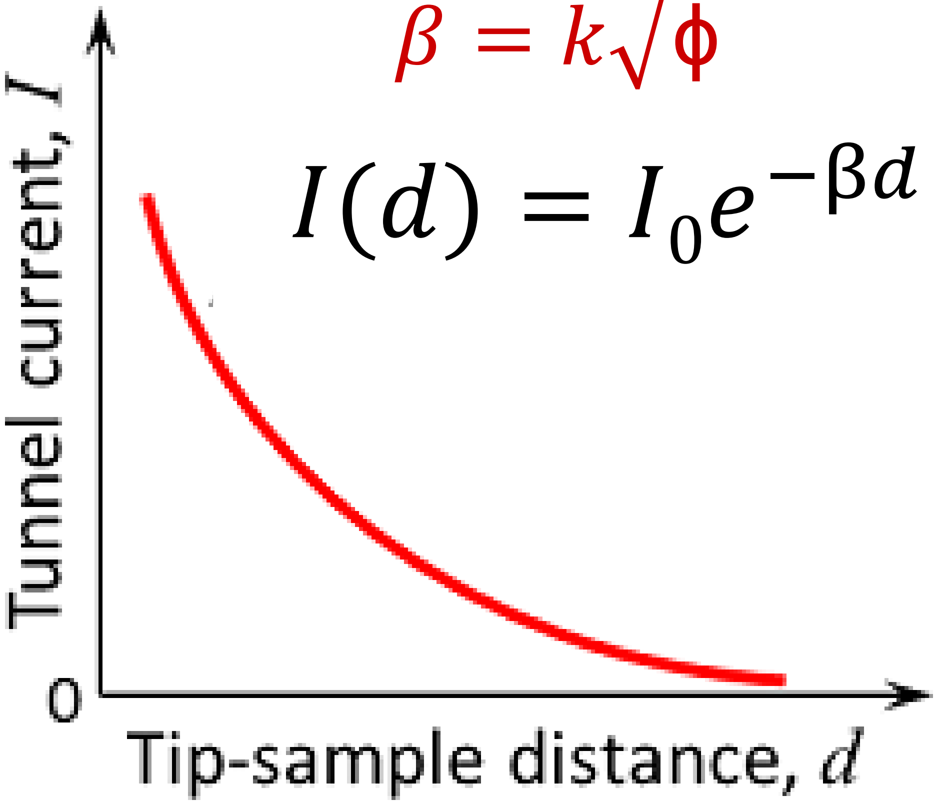
Tunnelling through a rectangular barrier…



β = constant

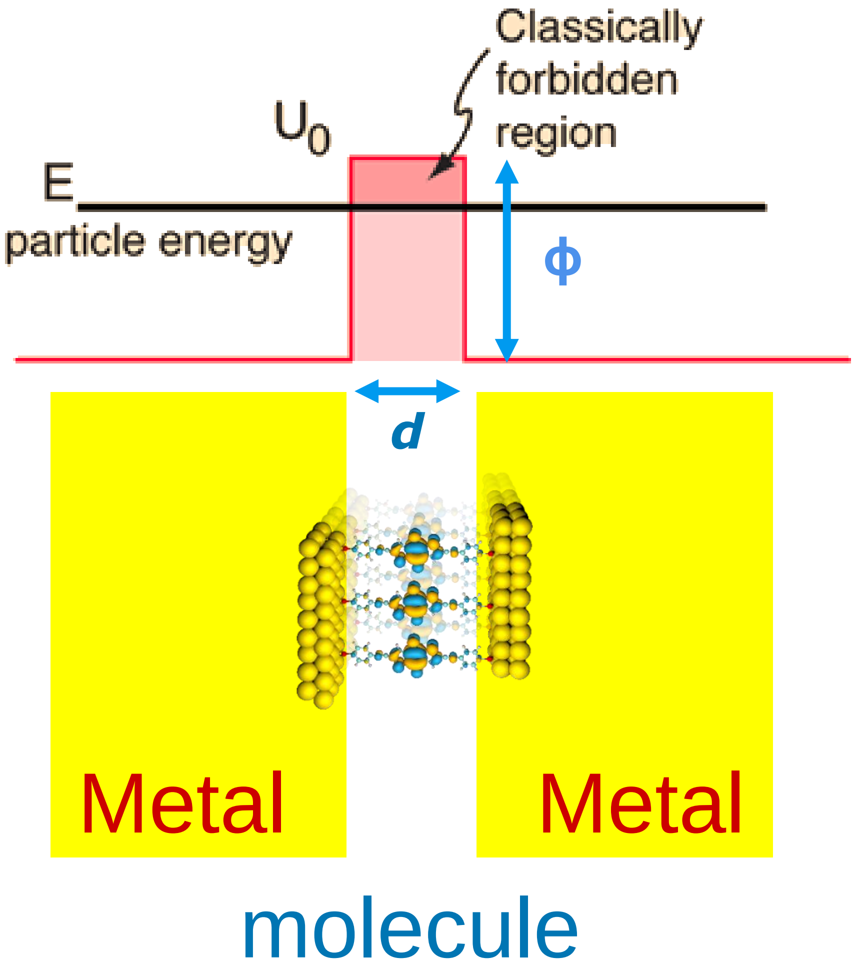
$\beta = k\sqrt{\phi}$

$I(d) = I_0 e^{-\beta d}$



Applying in Molecular Electronics…

Tunnelling through a molecular barrier…



β = constant

$$\beta = k\sqrt{\phi}$$

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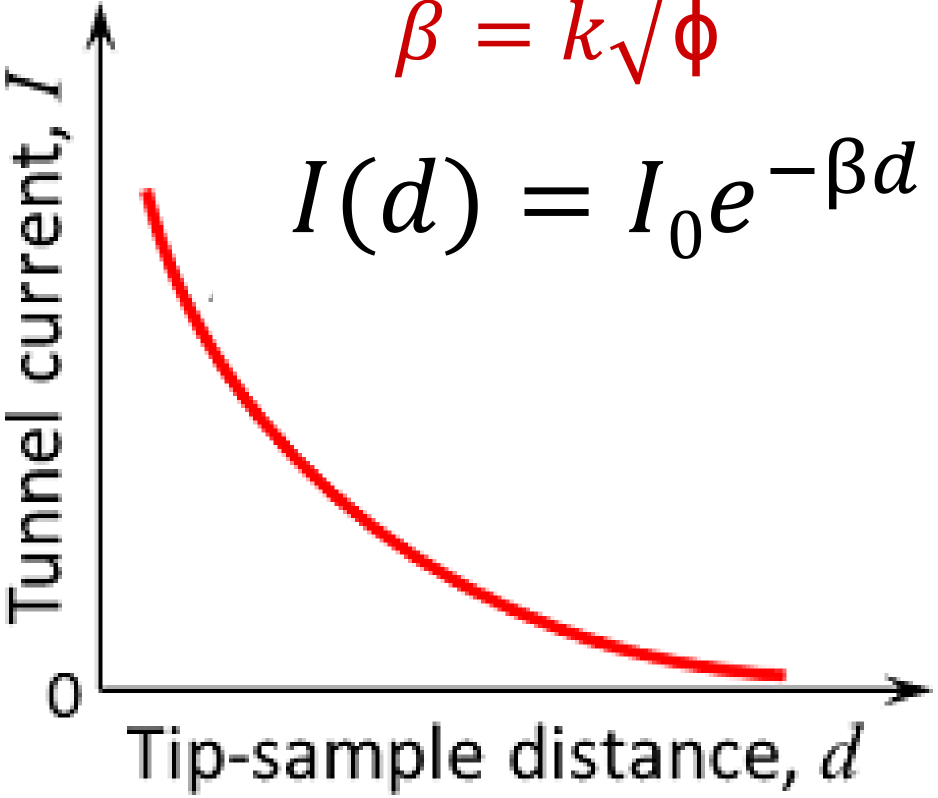


Literature examples

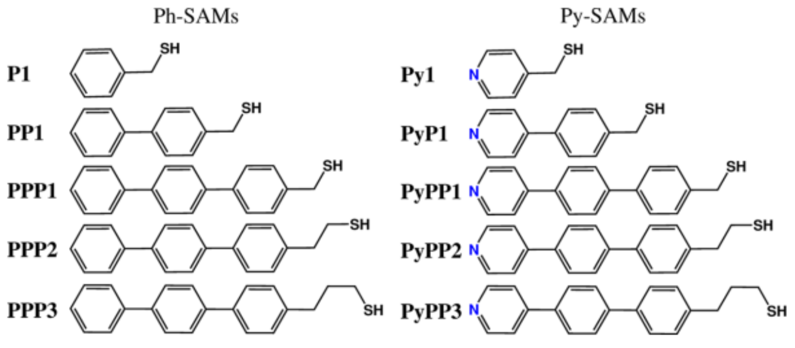
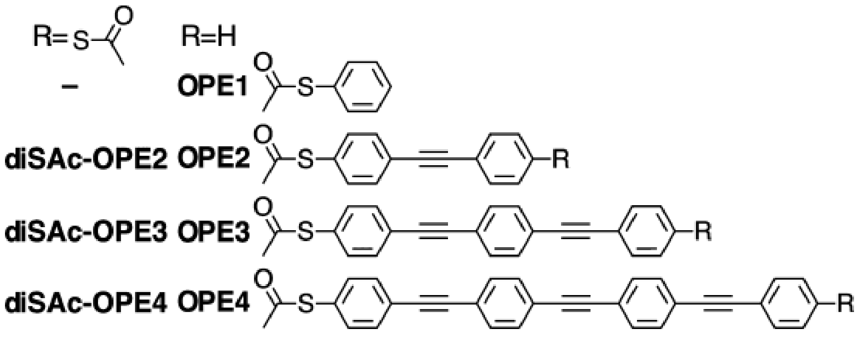


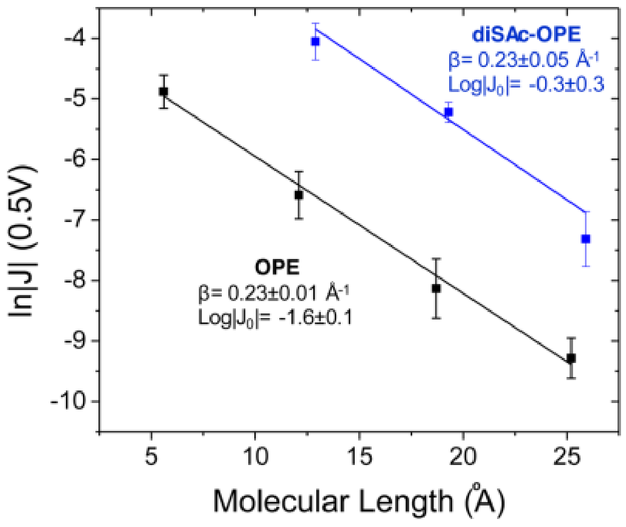
Table 1. Values of β and J_0 for Subsets and Combinations of the Ph-SAM and Py-SAM Series

trend	molecules	β ($Å^{-1}$)	J_0 (A/cm^2)
full series	Ph-SAM	0.44 ± 0.04	1.18 ± 1.44
	Py-SAM	0.42 ± 0.08	2.46 ± 3.00
odd only	P1, PP1, PPP1, PPP3	0.47 ± 0.04	1.45 ± 1.43
	Py1, PyP1, PyPP1, PyPP3	0.40 ± 0.07	2.35 ± 2.77
aryl	P1, PP1, PPP1	0.46 ± 0.07	1.32 ± 1.85
	Py1, PyP1, PyPP1	0.32 ± 0.17	1.11 ± 6.00
alkyl	PPP1, PPP2, PPP3	0.56 ± 0.41	n.d.
	PyPP1, PyPP2, PyPPP3	0.36 ± 0.41	n.d.

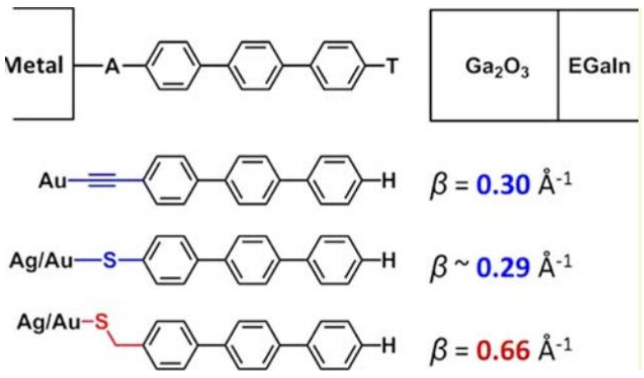
J. Phys. Chem. C 2013, 117, 11367−11376

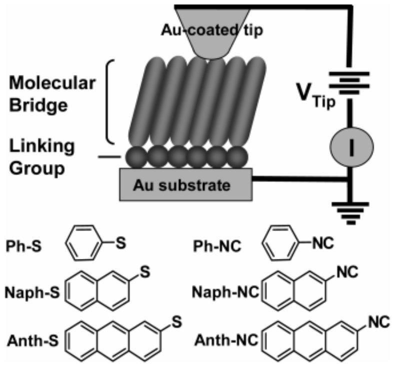
β = constant

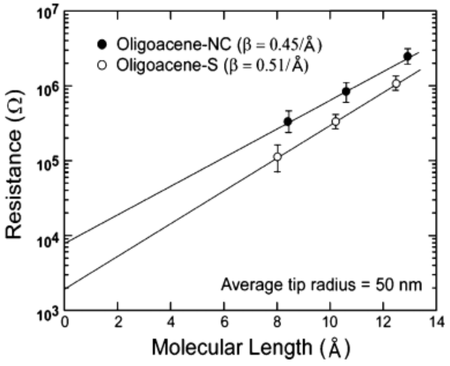




J. Phys. Chem. C 2016, 120, 20437−20445

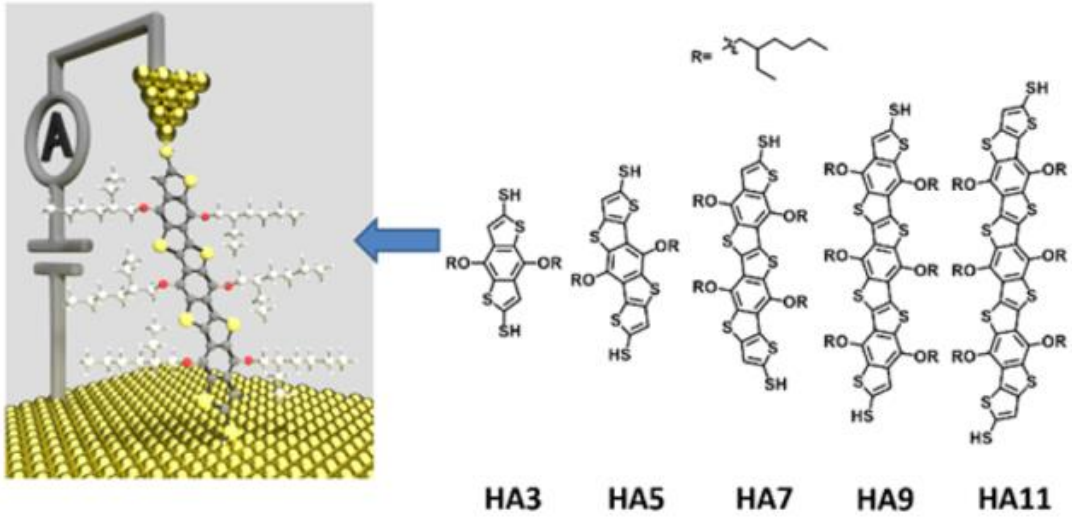






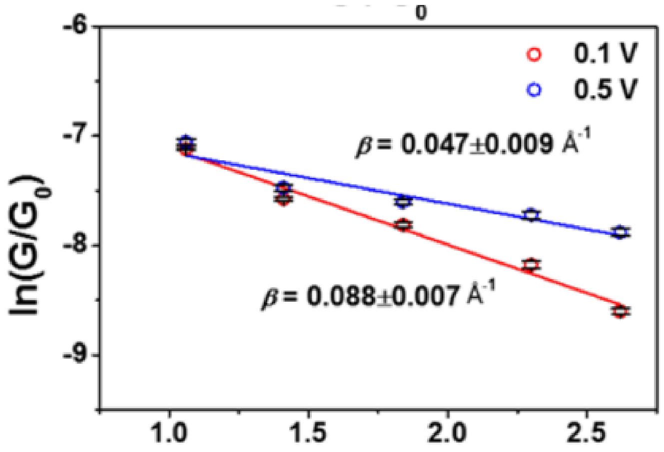
J. AM. CHEM. SOC. 2006, *128*, 4970−4971

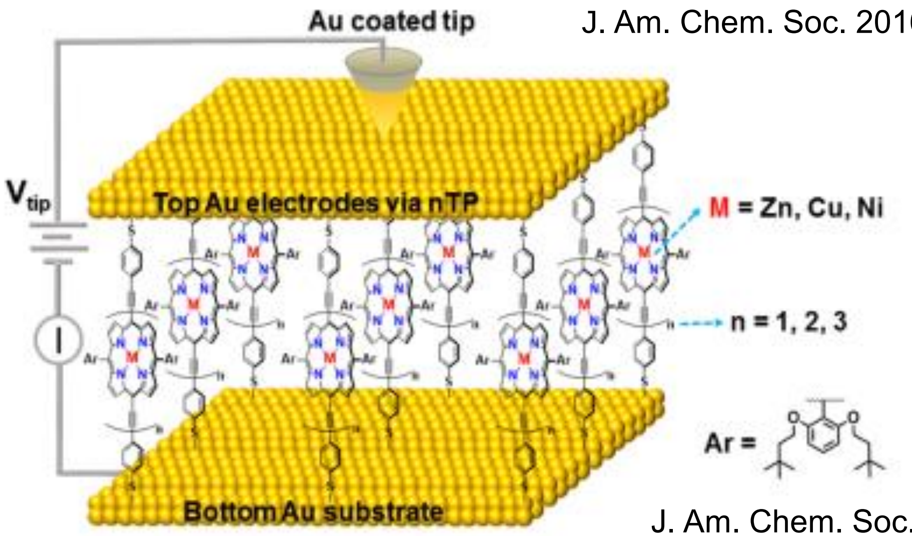
Literature examples

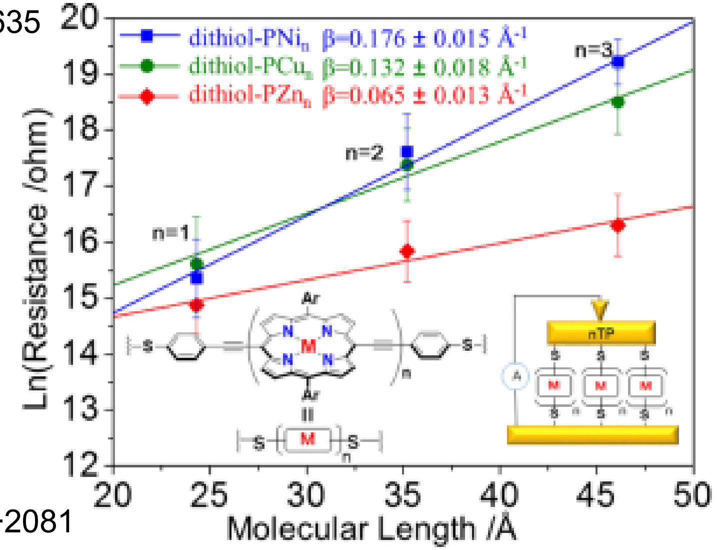


J. Am. Chem. Soc. 2016, 138, 10630−10635

β ~ 0

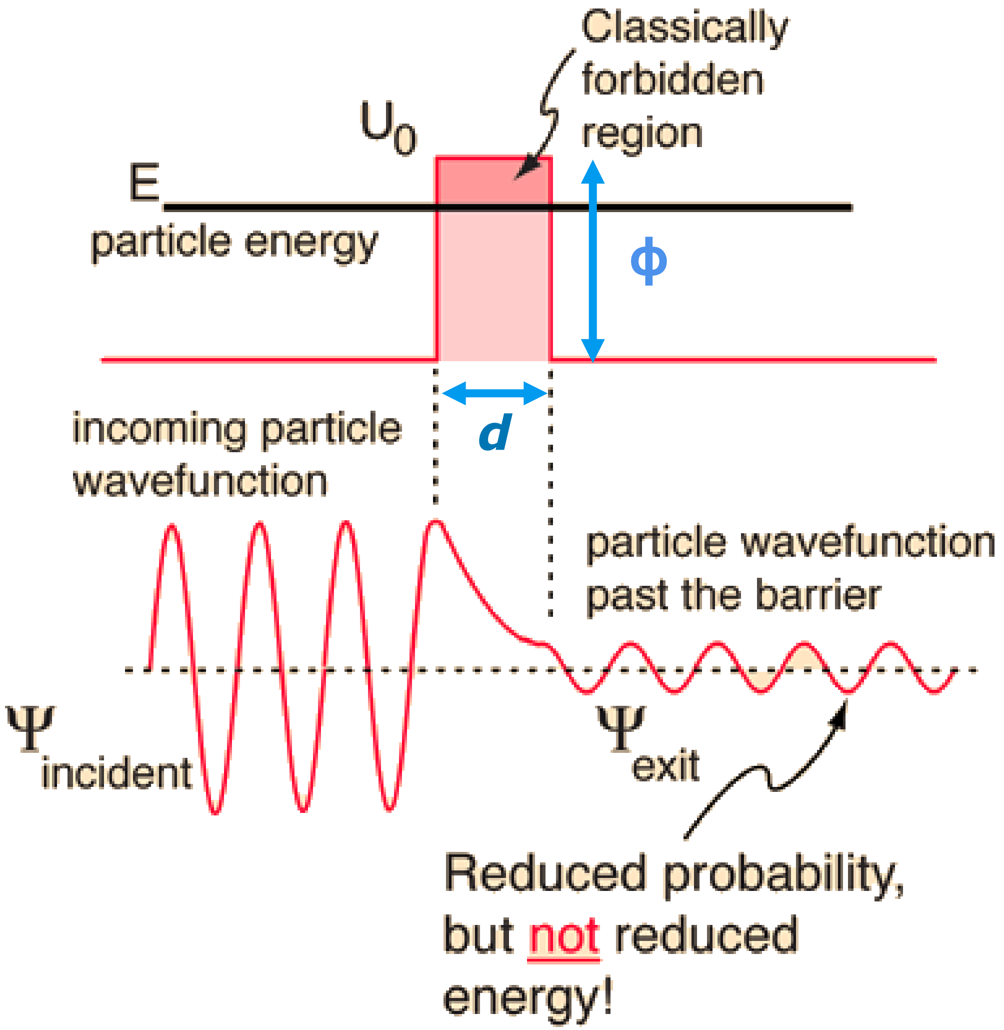






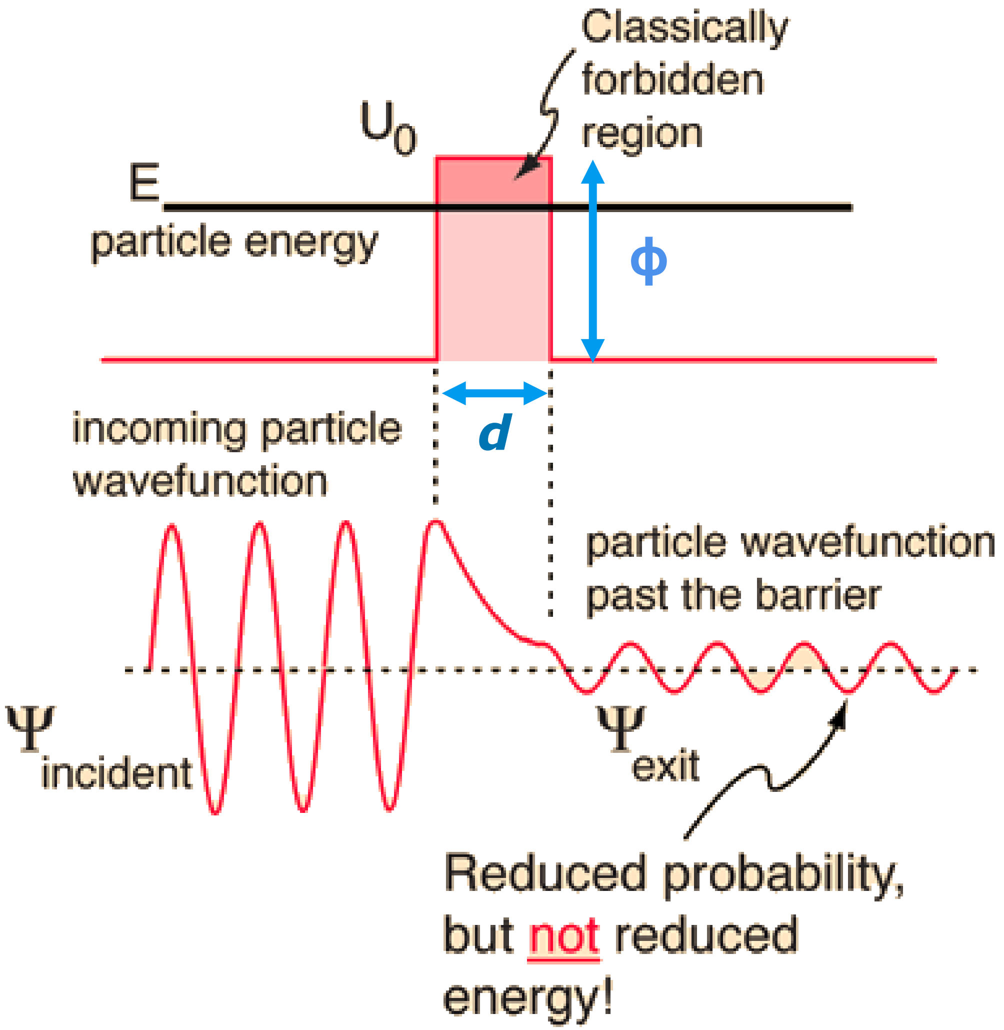
J. Am. Chem. Soc. 2016, 138, 2078−2081

Common Claim!



β = constant

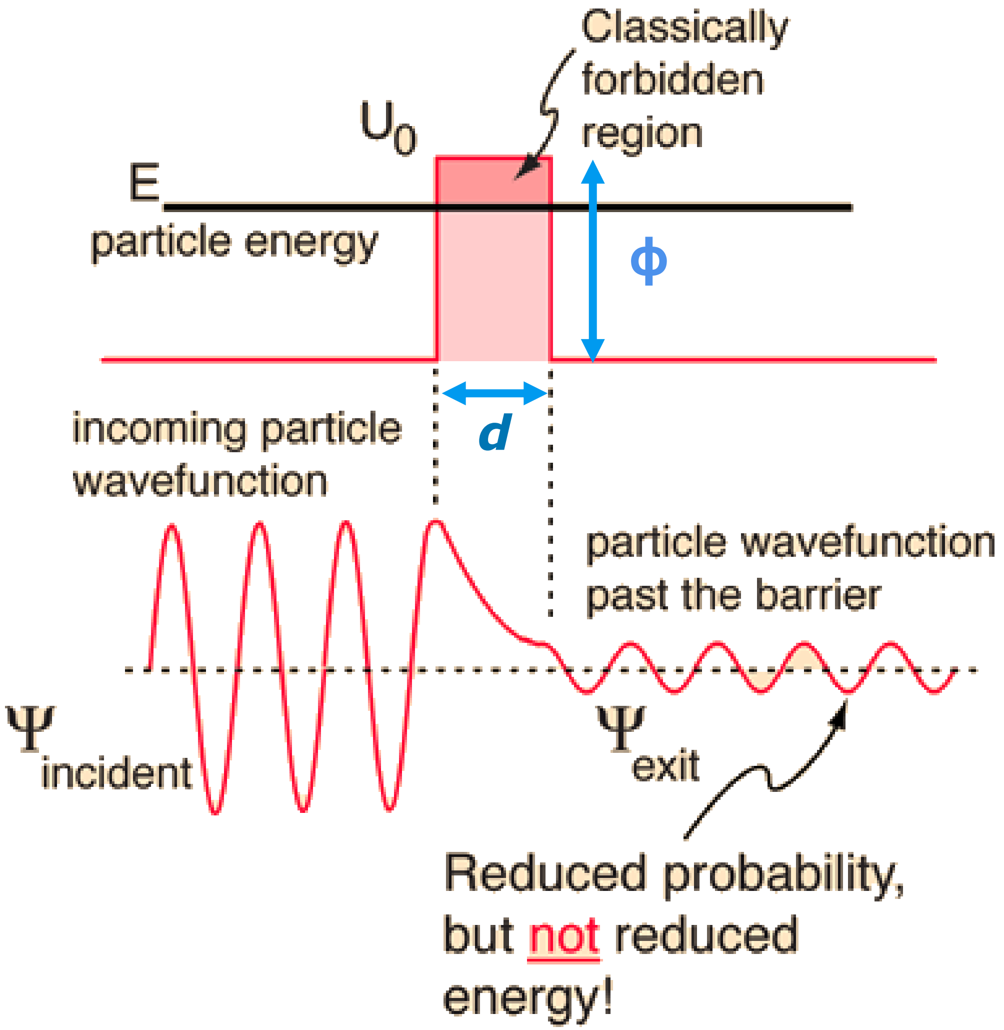
Common Assumption!



β = constant

$\rightarrow \phi$ = constant

Common Assumption!



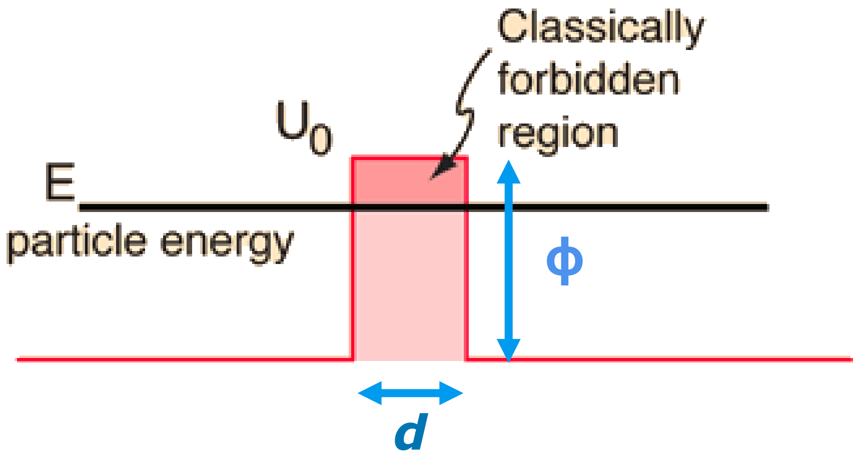
β = constant

$\rightarrow \phi$ = constant

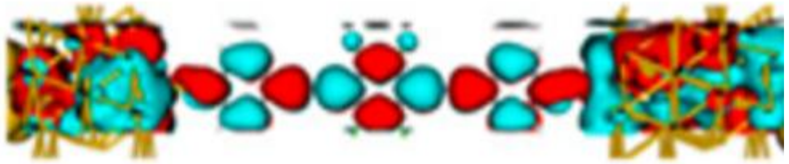
But we know E_g changes!

$$I(d) = I_0 e^{-\beta d}$$

Common Assumption!



- So there should be **fermi-pinning**
  - i.e., ($E_{HOMO/LUMO}$ - E_{Fermi}) = constant
  - hybridization between the molecule and the electrodes



β = constant

$\rightarrow \phi$ = constant

So ϕ would change!

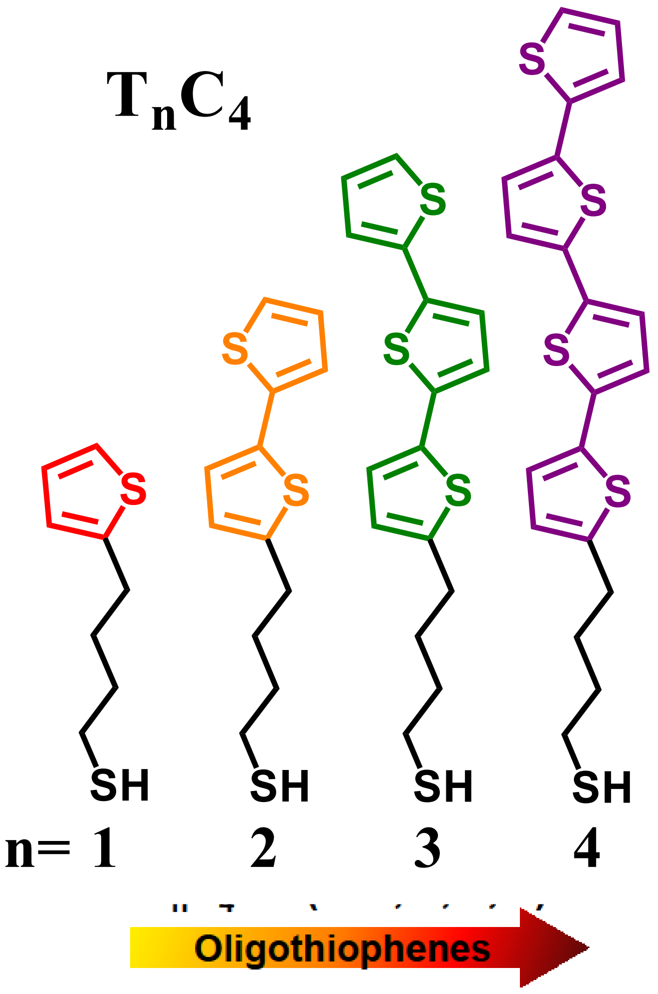
$$I(d) = I_0 e^{-\beta d}$$

J. Phys. Chem. Lett. 9, 9, 2394-2403

Goals!

- Exclude the effect of **Fermi pinning**
- Understand the influence of barrier height on current

Target system

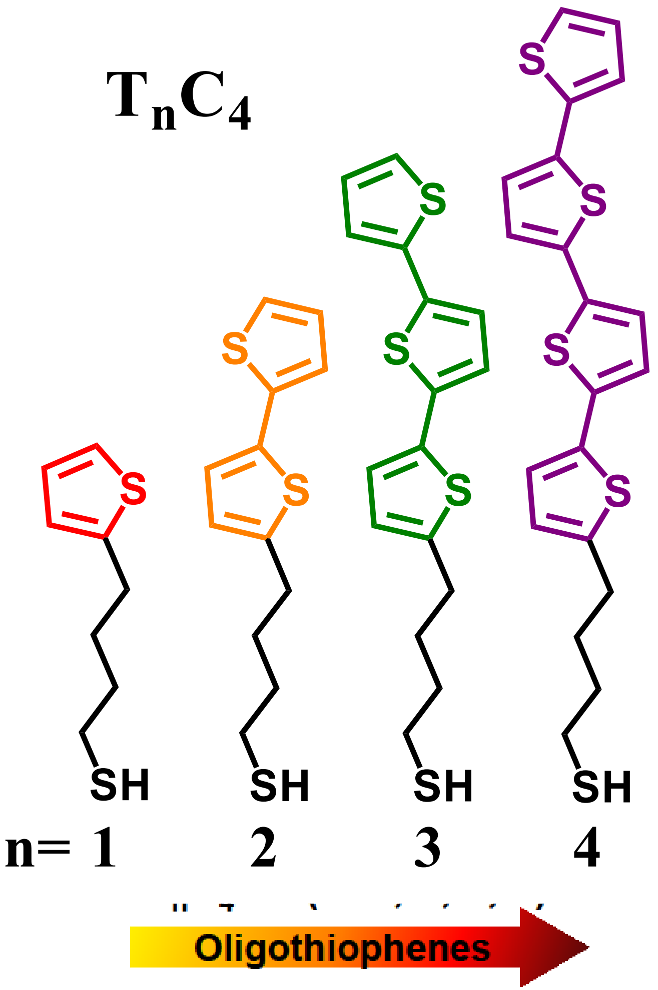


Increase in Tunneling Distance (d)

Decrease in Barrier Height (ϕ)

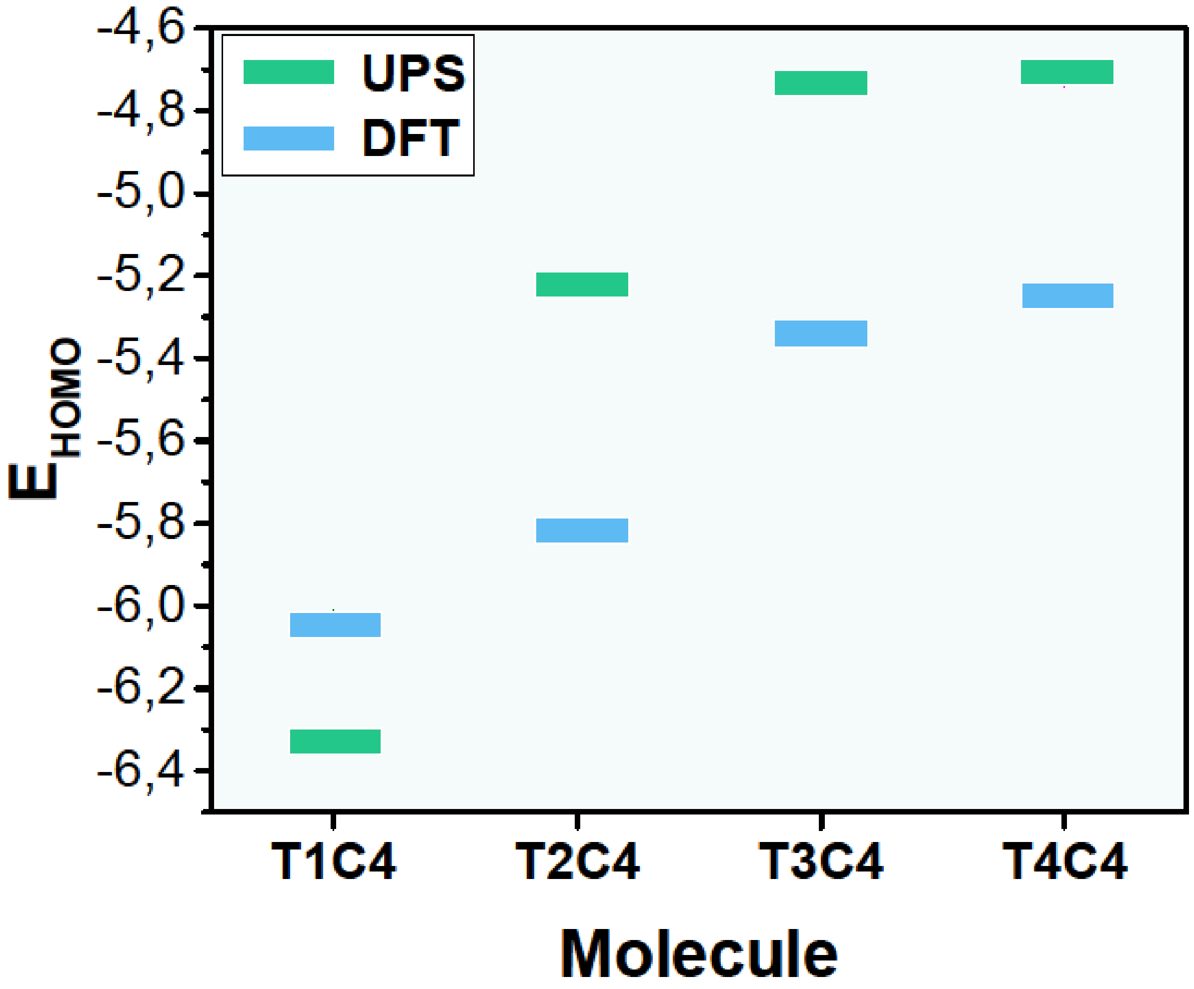
Oligothiophene series

Target system: Oligothiophene series

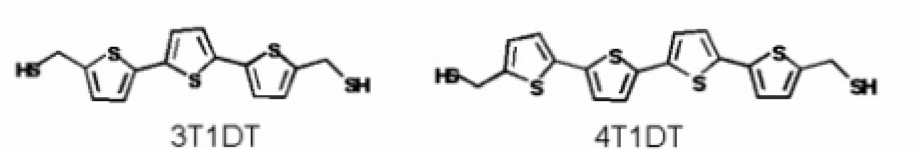


Increase in Tunneling Distance (d)

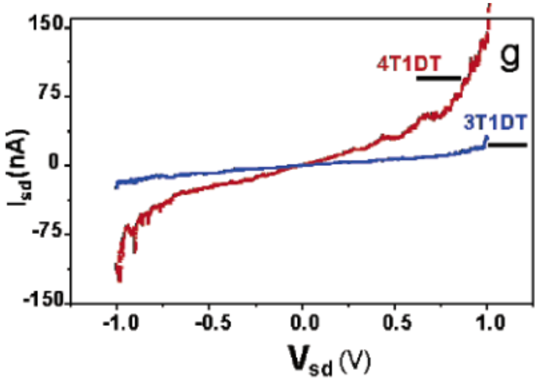
Decrease in Barrier Height (ϕ)



Why Oligothiophene?



10.1021/nl050860j



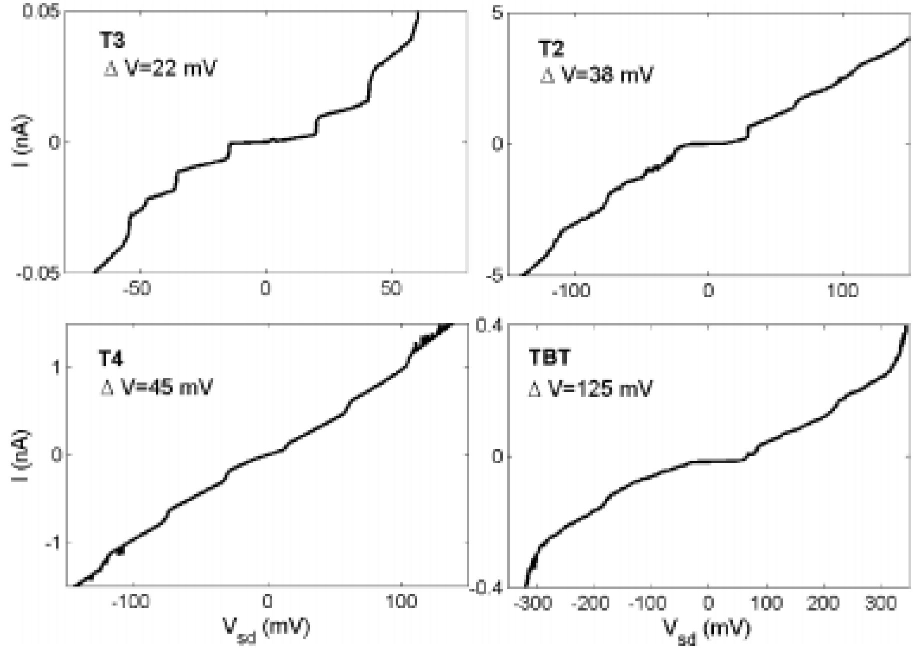
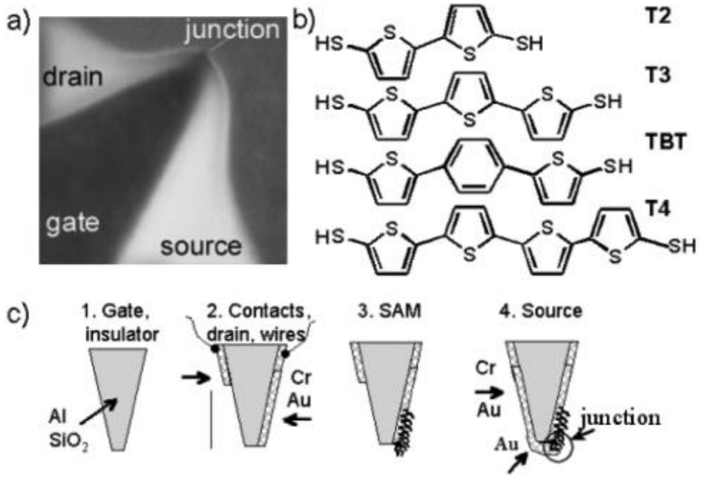
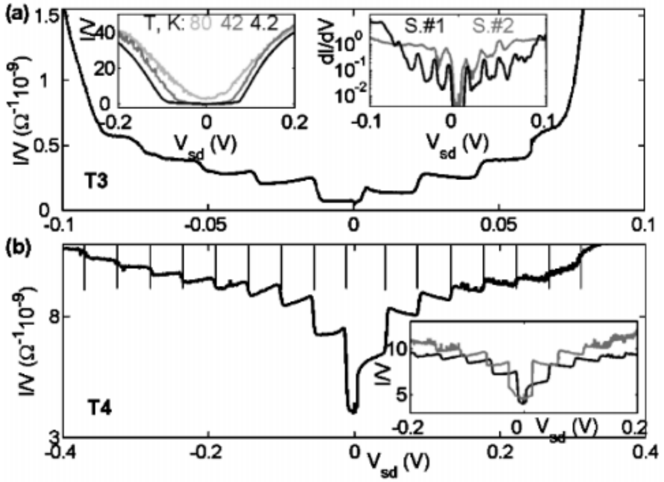


Figure 3. Typical *I–V* curves measured on molecular junctions. $T = 4.2$ K.

DOI: 10.1103/PhysRevLett.88.226801





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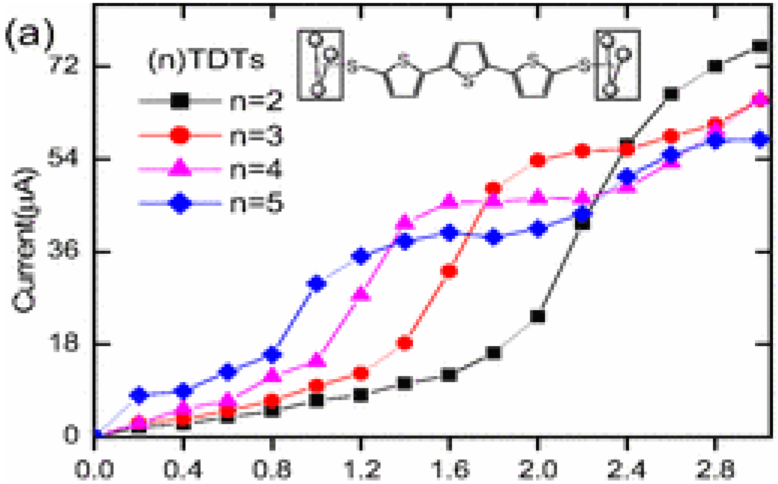
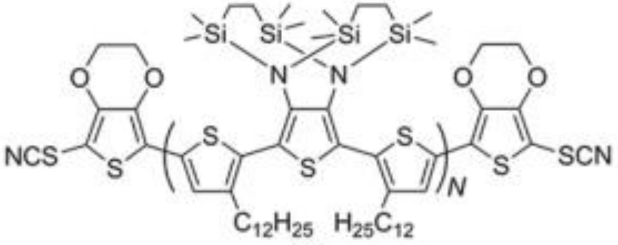
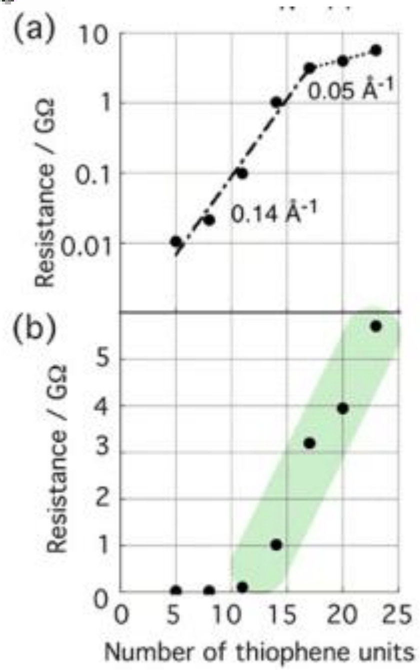
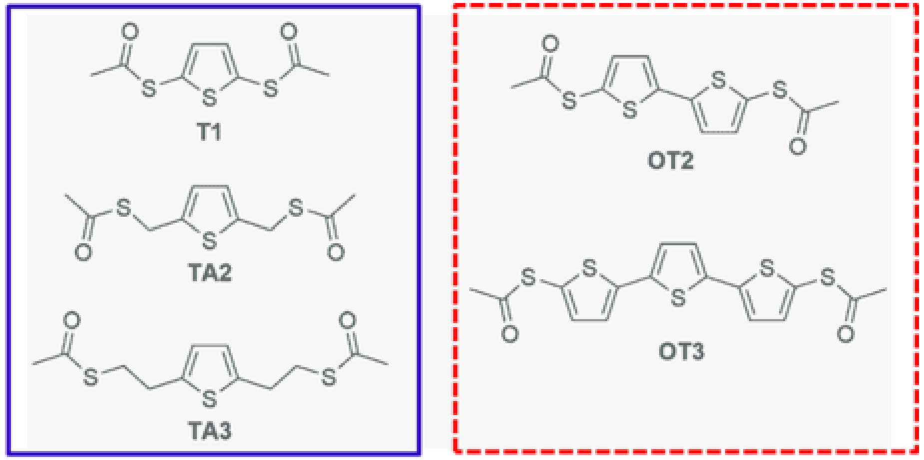


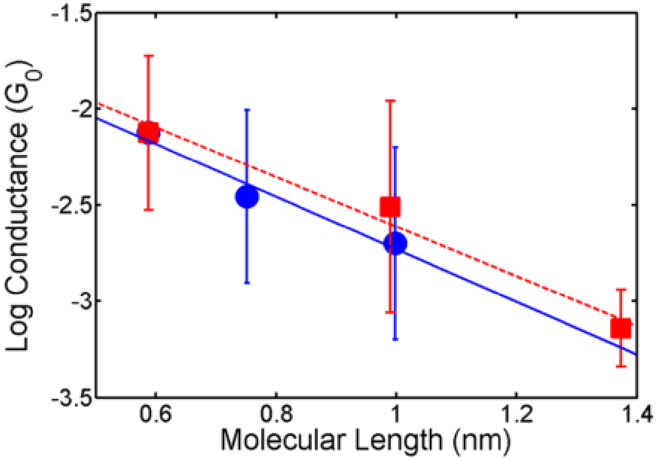
Phys. Rev. B 75, 245407



14 *N* = 1-7



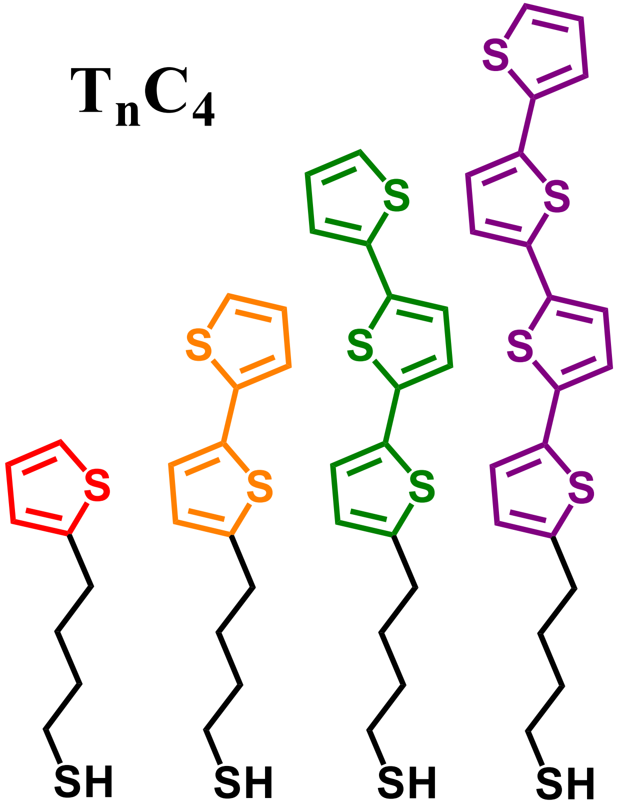




dx.doi.org/10.1021/cm504254n | *Chem. Mater.* 2014, 26, 7229−7235

Target system

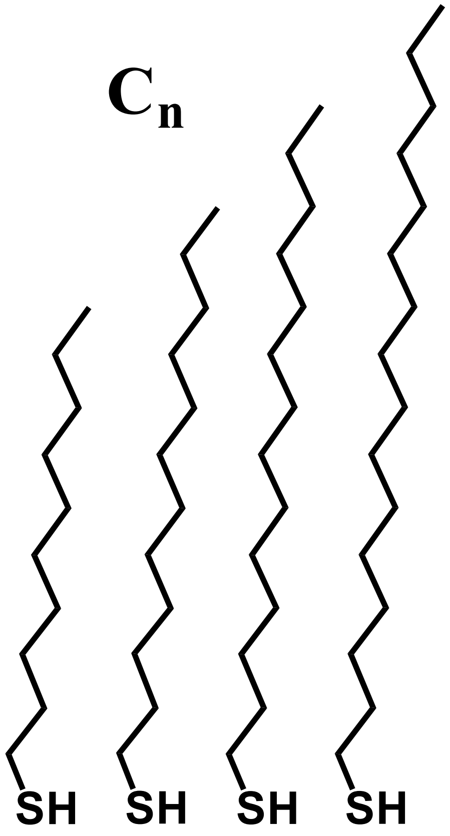
T_nC_4



n= 1 2 3 4

Oligothiophene series
(alkanes for reference)

C_n



n= 10 12 14 16

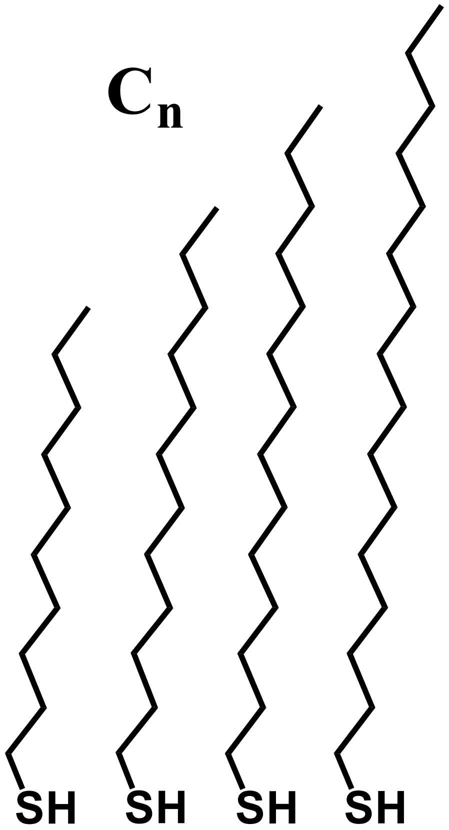
Oligothiophenes

Increase in Tunneling Distance (d)
Decrease in Barrier Height (ϕ)

Alkanes

Increase in Tunneling Distance (d)
Constant Barrier Height (ϕ)

Observation - Alkanethiols



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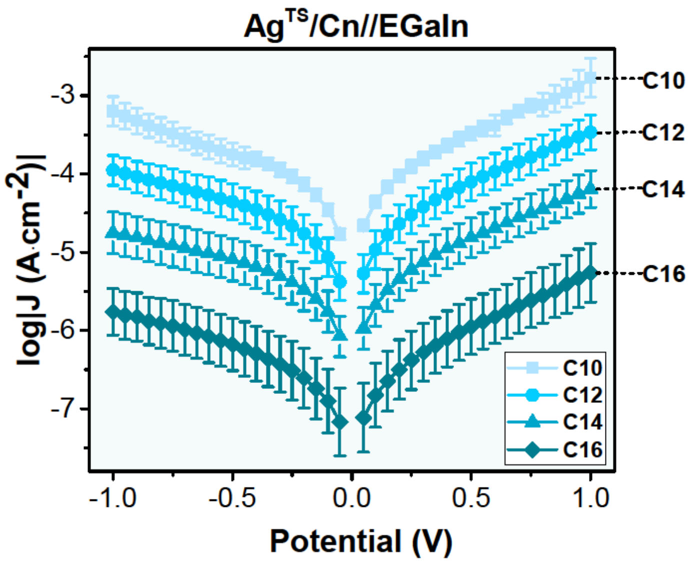
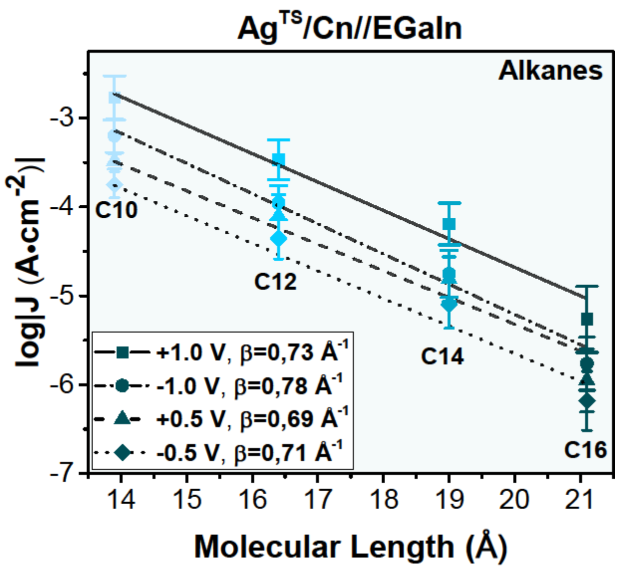
Alkanes

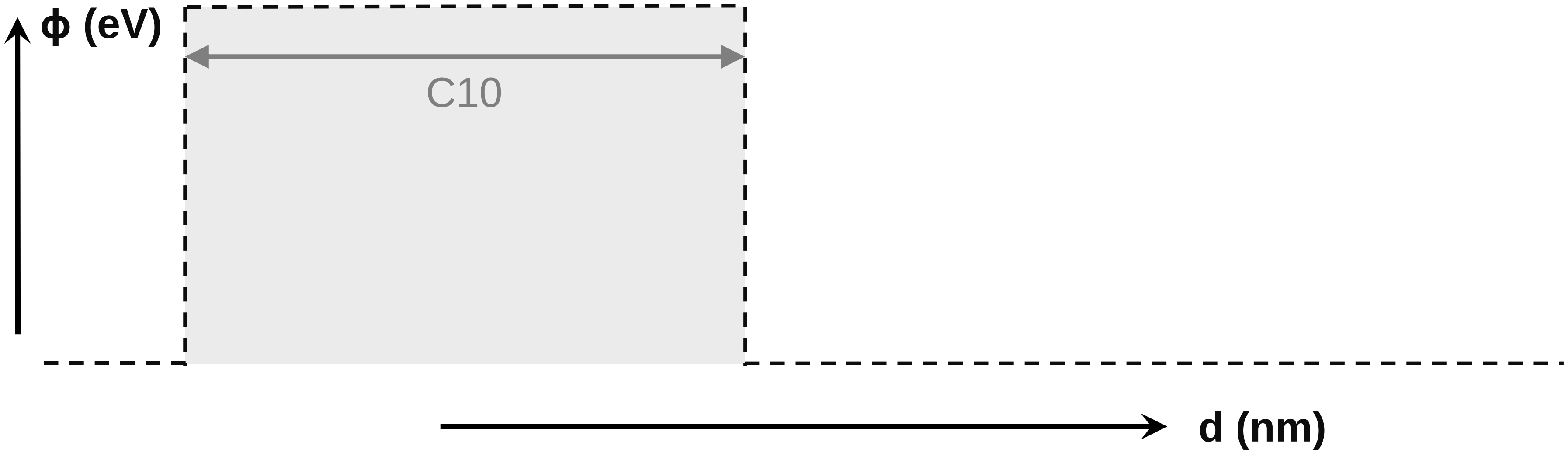
Increase in Tunneling Distance (d)

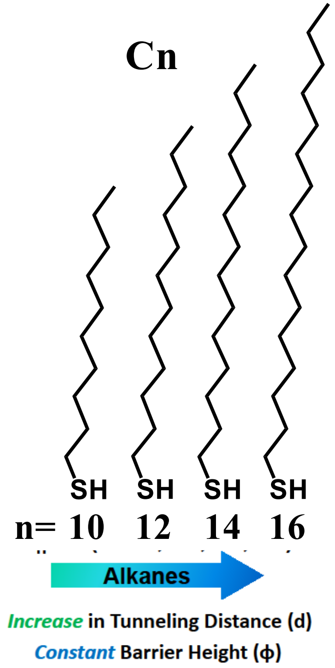
Constant Barrier Height (ϕ)





Shape of potential barriers

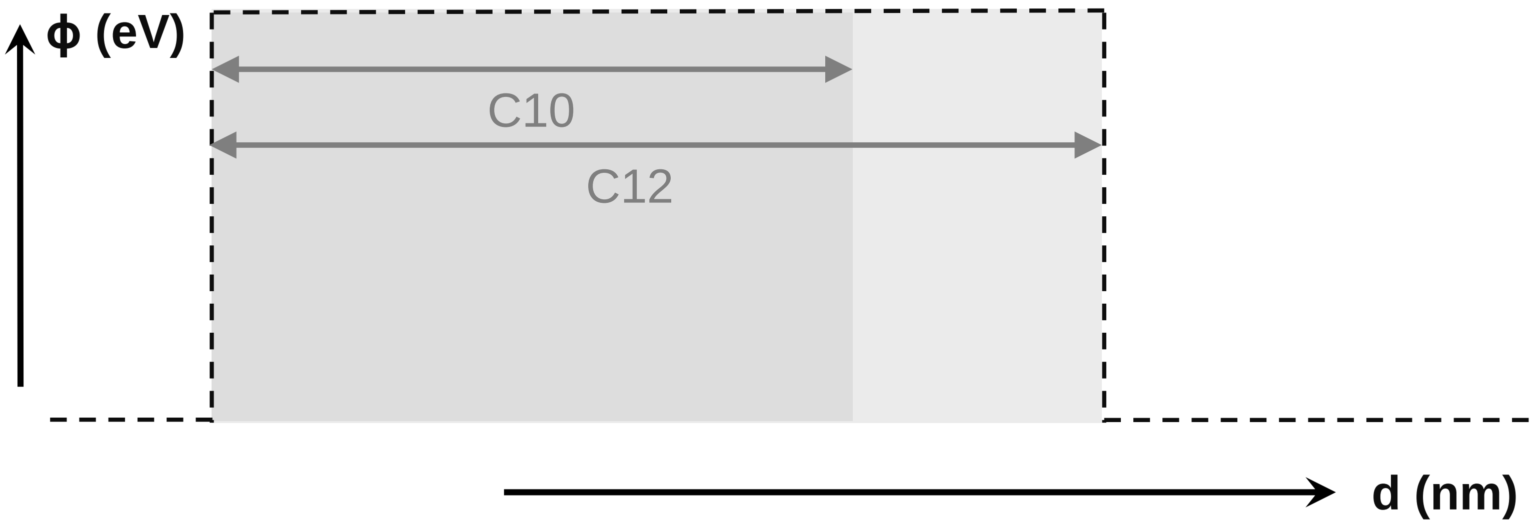


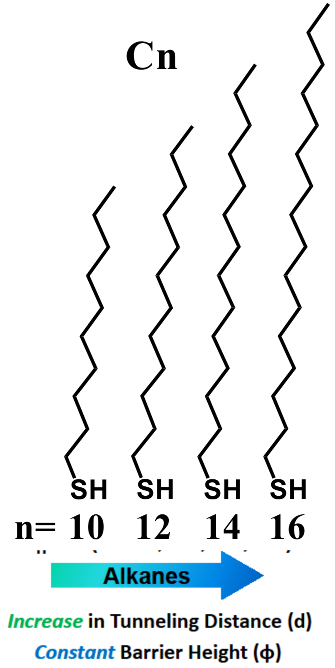


Single Rectangular Barrier

$$I(d) = I_0 e^{-\beta d} \qquad (\beta = \text{constant})$$

Shape of potential barriers





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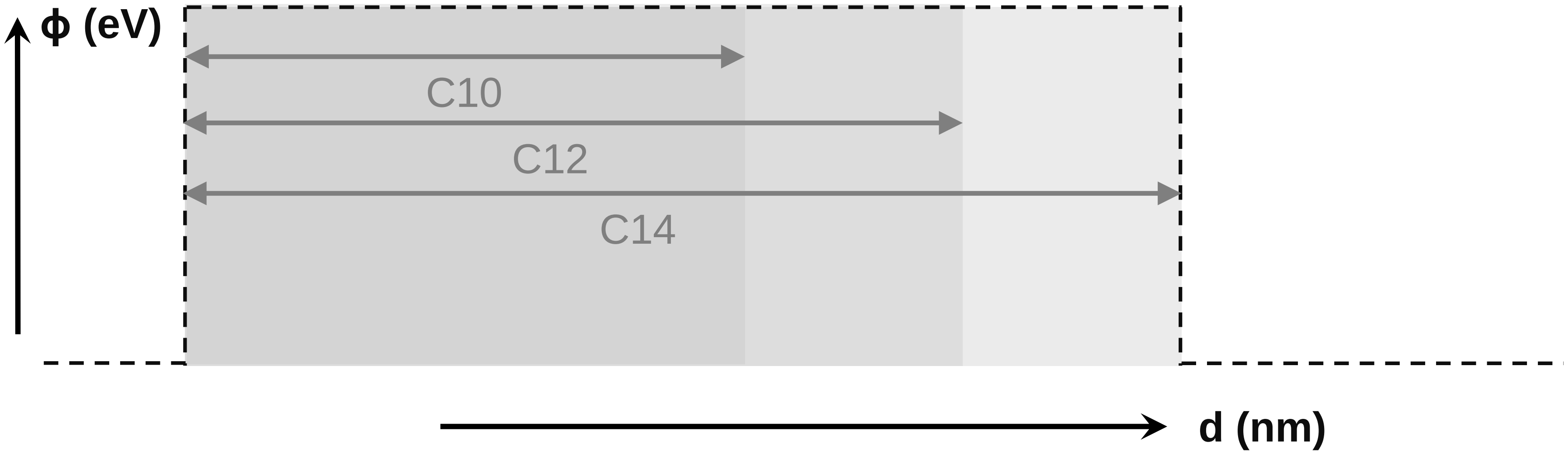

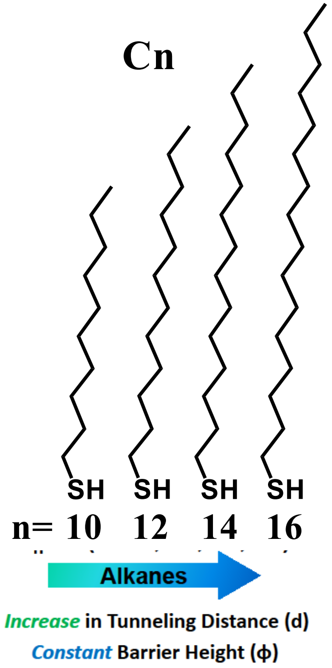

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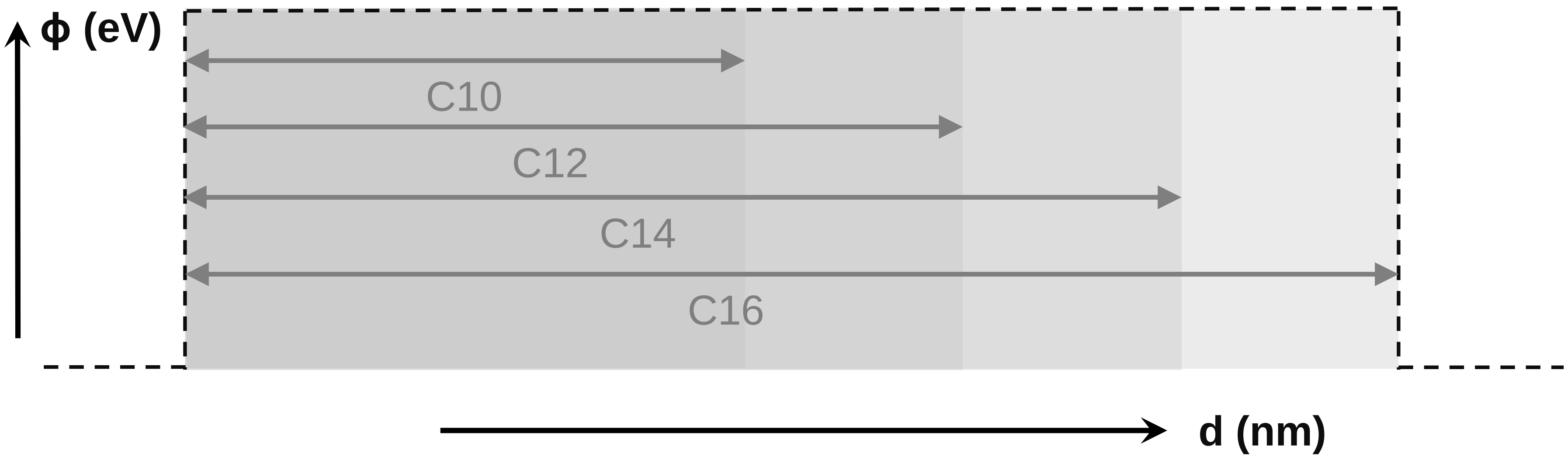

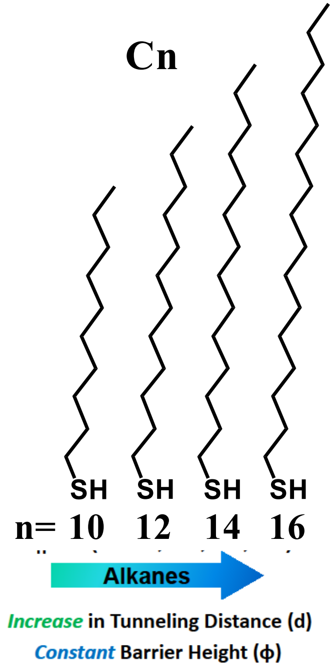

Single Rectangular Barrier

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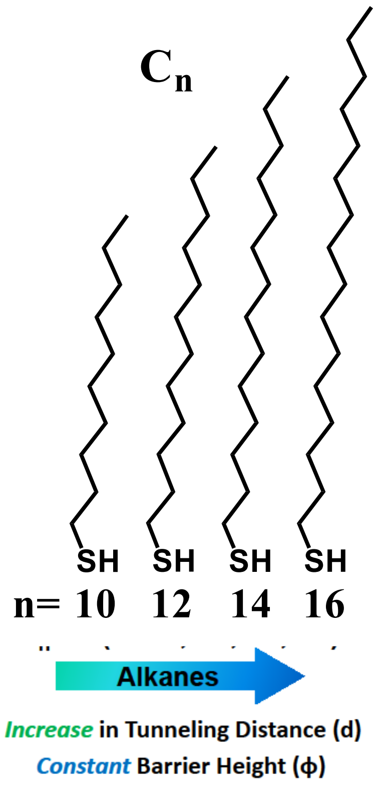
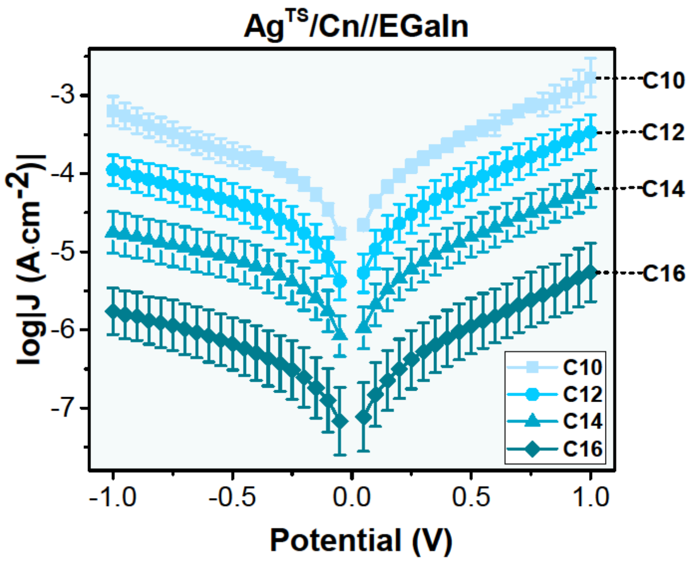
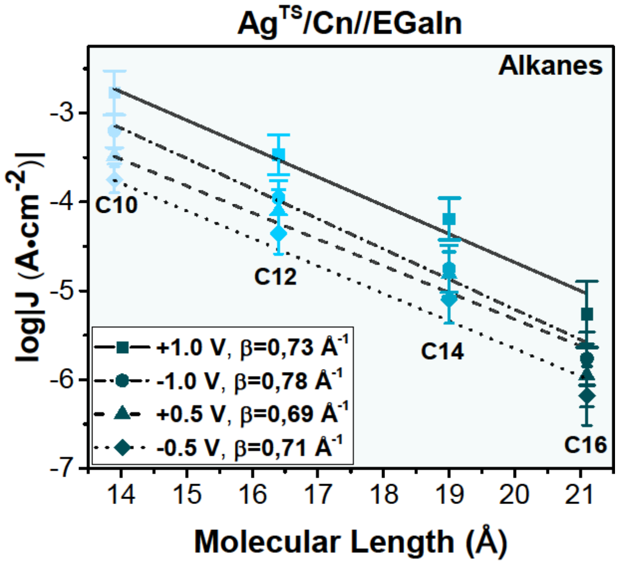
Observation - Alkanethiols

Made sense!

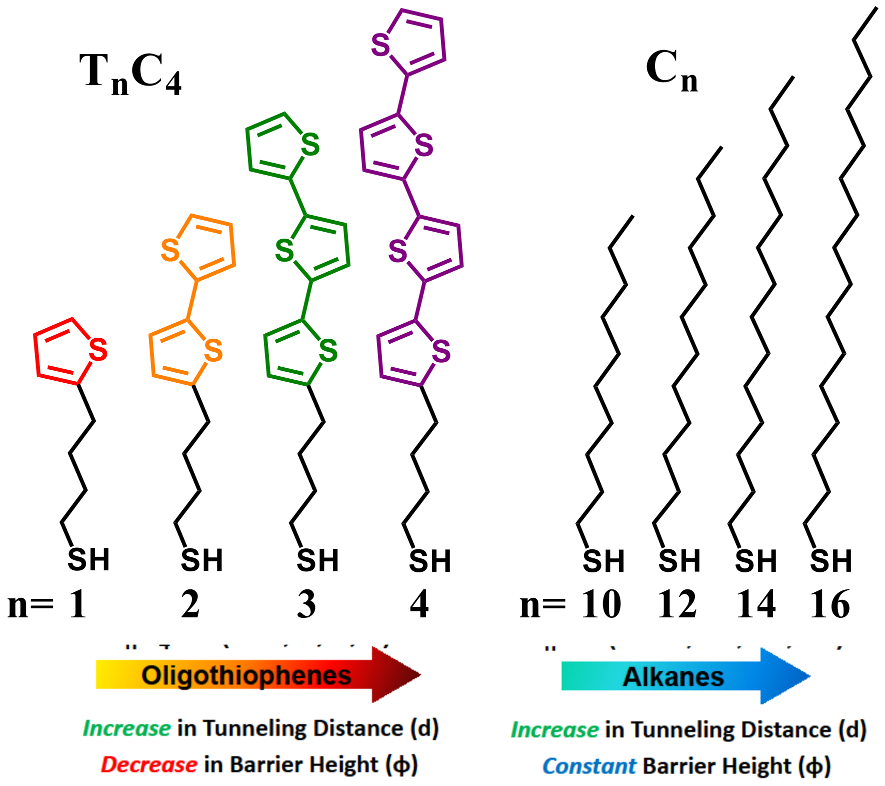


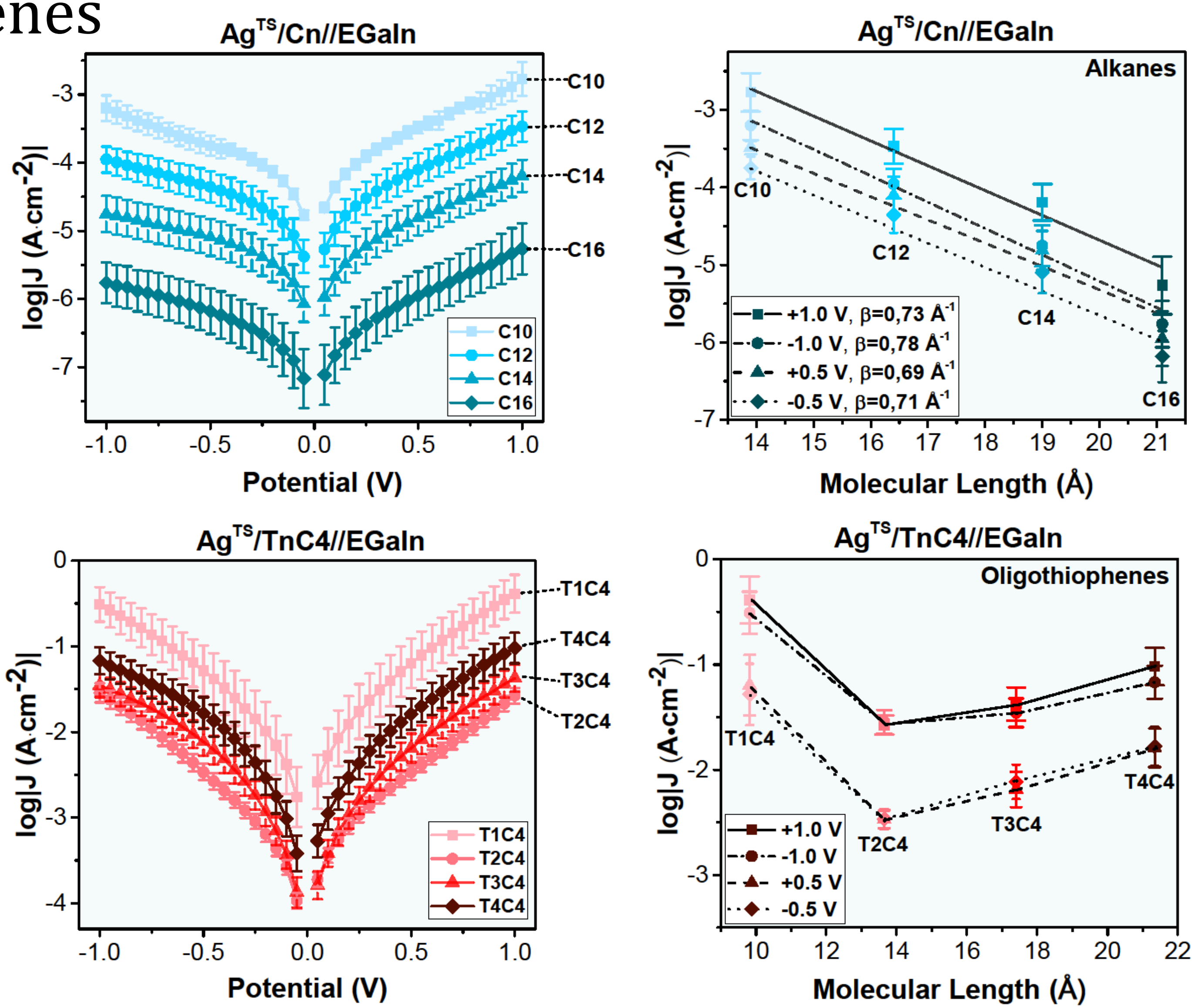




Observation - Oligothiophenes

Made NO sense!

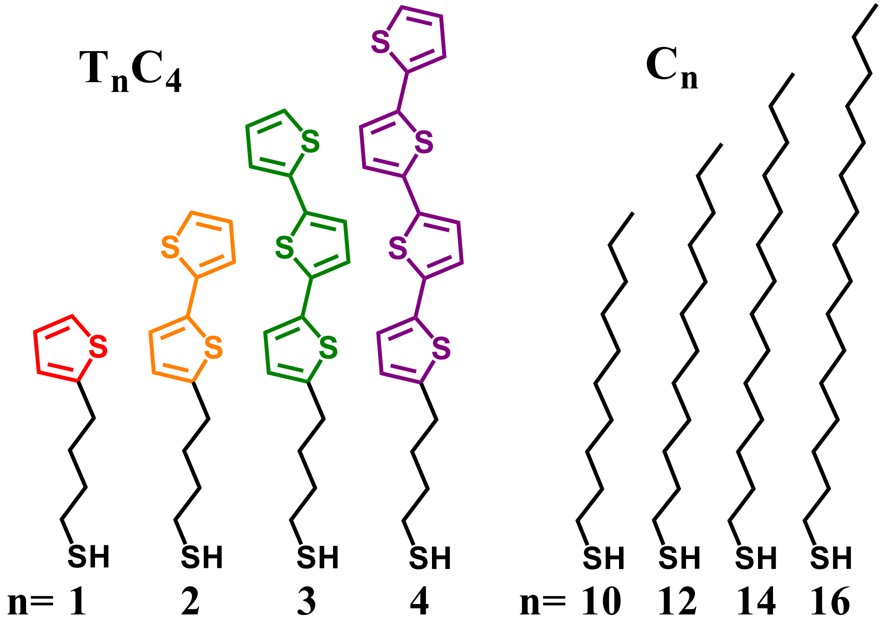




Observation - Oligothiophenes

Made NO sense!

T1C4 > T4C4 > T3C4 > T2C4



Oligothiophenes

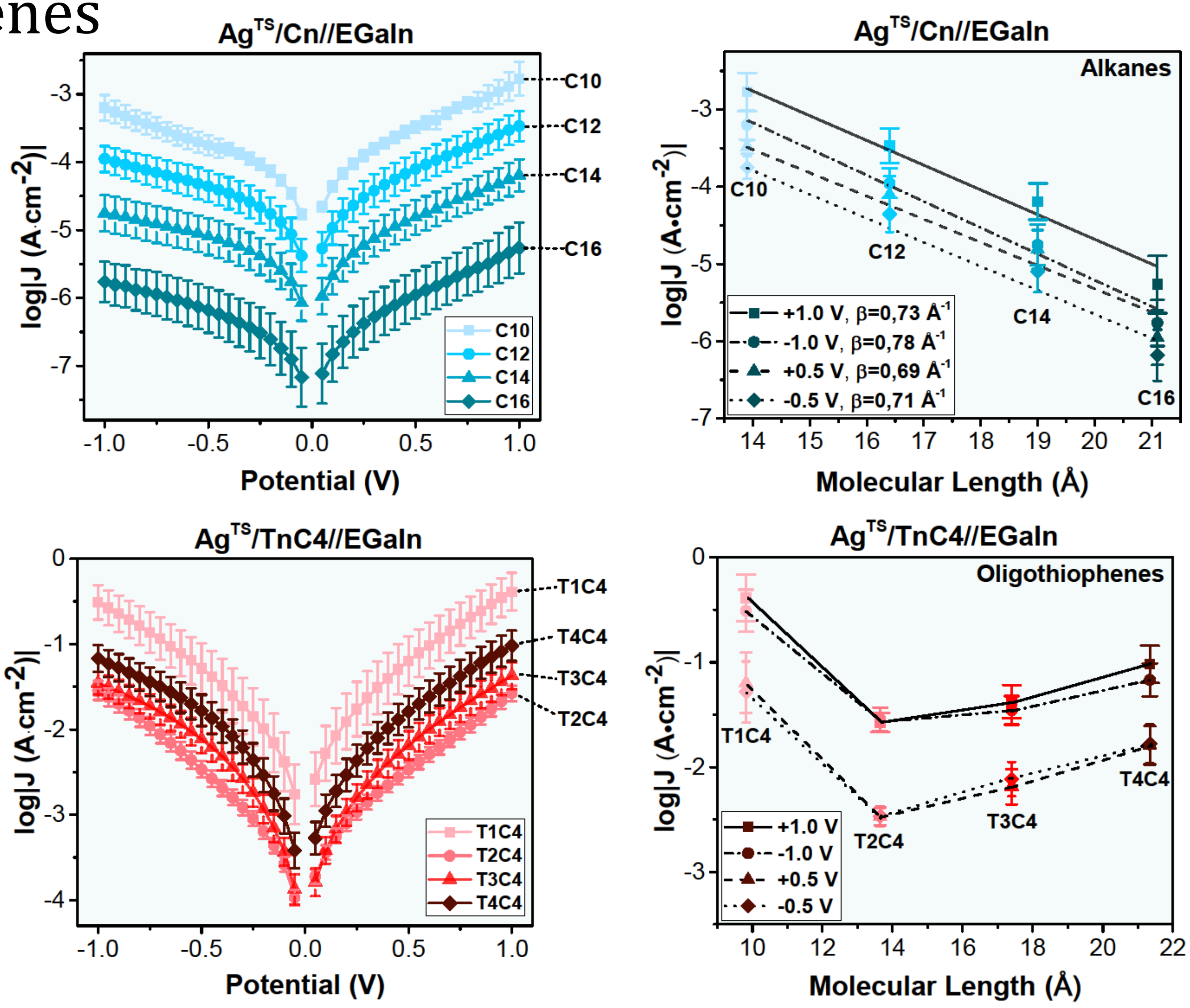
Increase in Tunneling Distance (d)

Decrease in Barrier Height (ϕ)

Alkanes

Increase in Tunneling Distance (d)

Constant Barrier Height (ϕ)

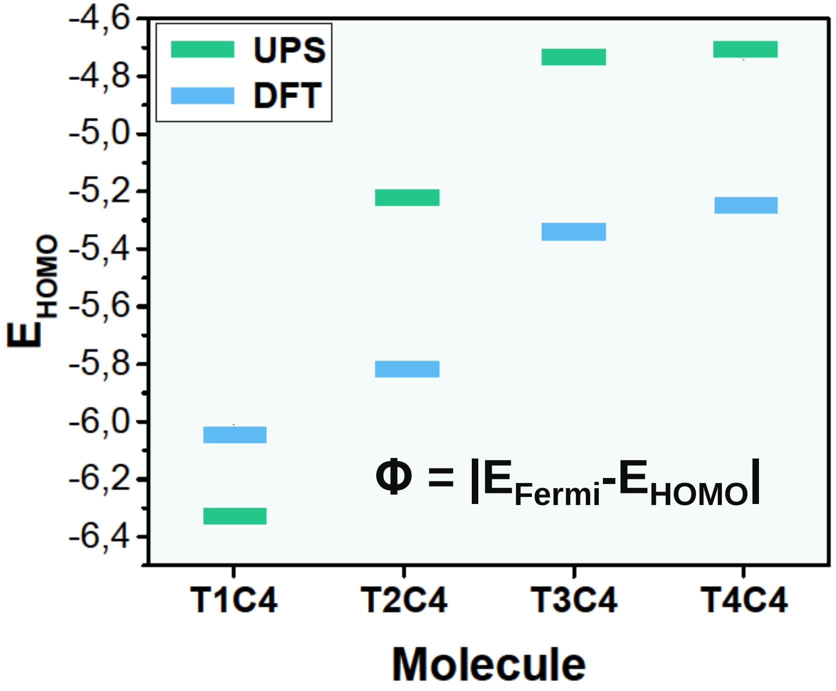


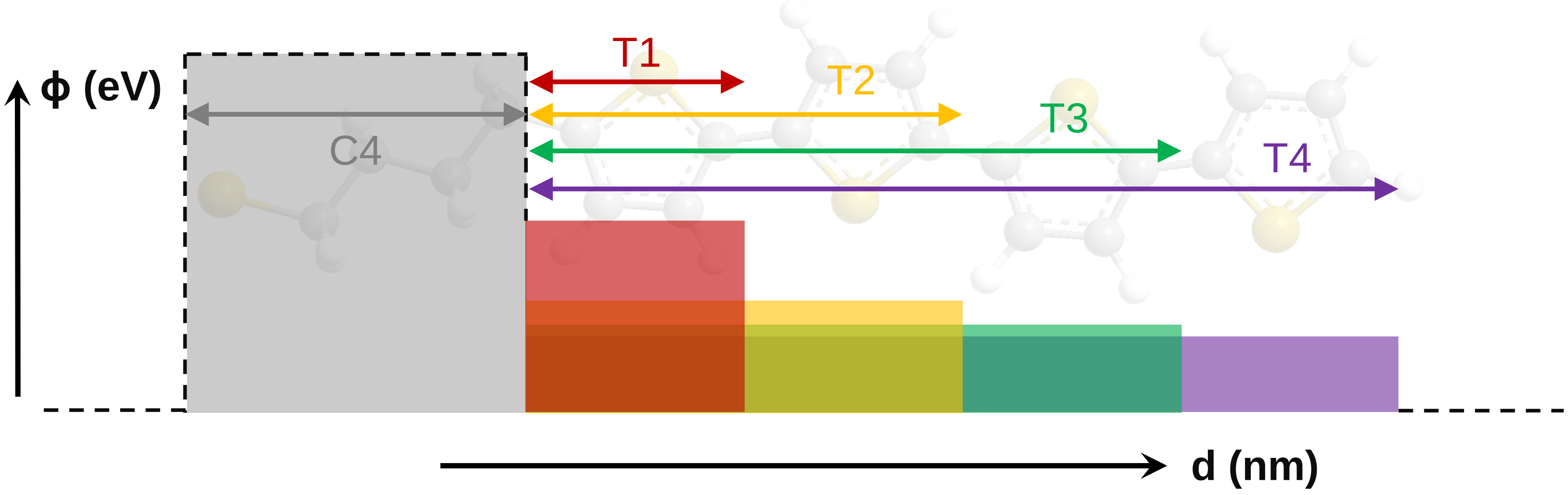
Shape of potential barriers

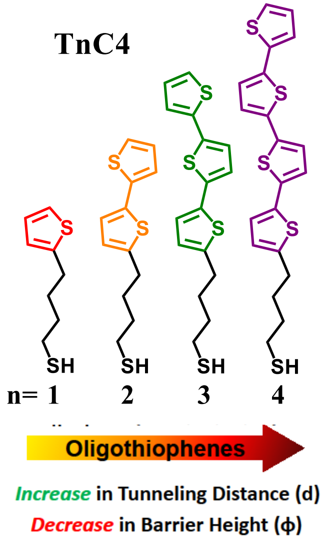
Made NO sense!

T1C4 > T4C4 > T3C4 > T2C4

- **Two Barrier Model** taking into account:
  1. increasing barrier width
  2. decreasing barrier height







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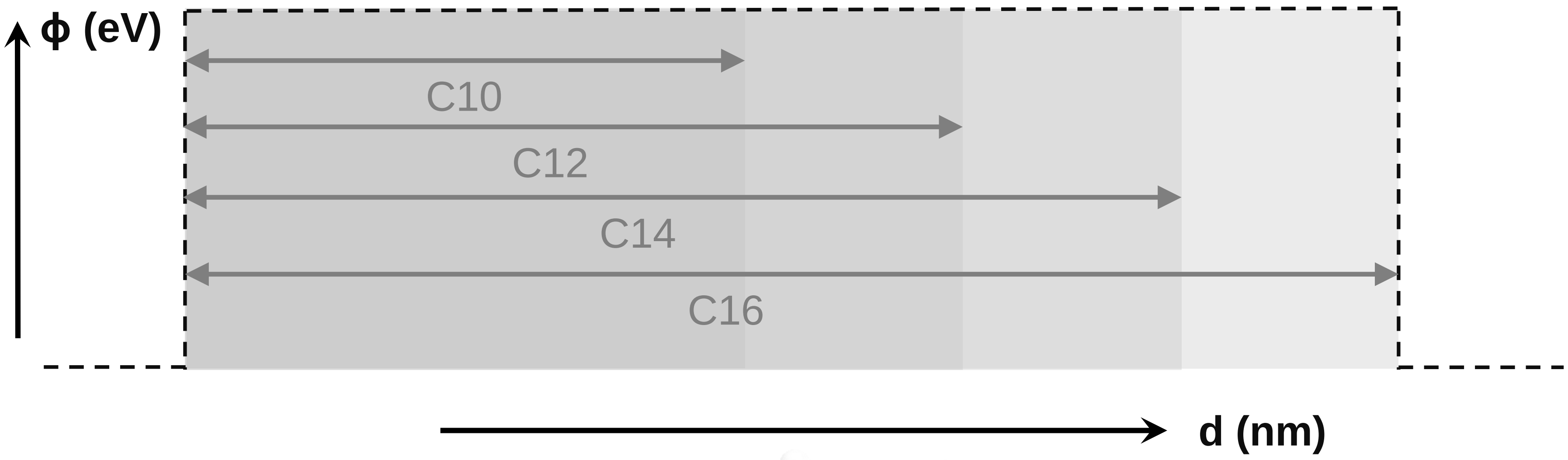
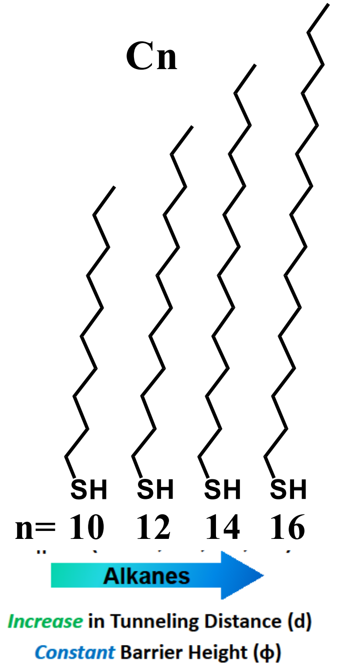
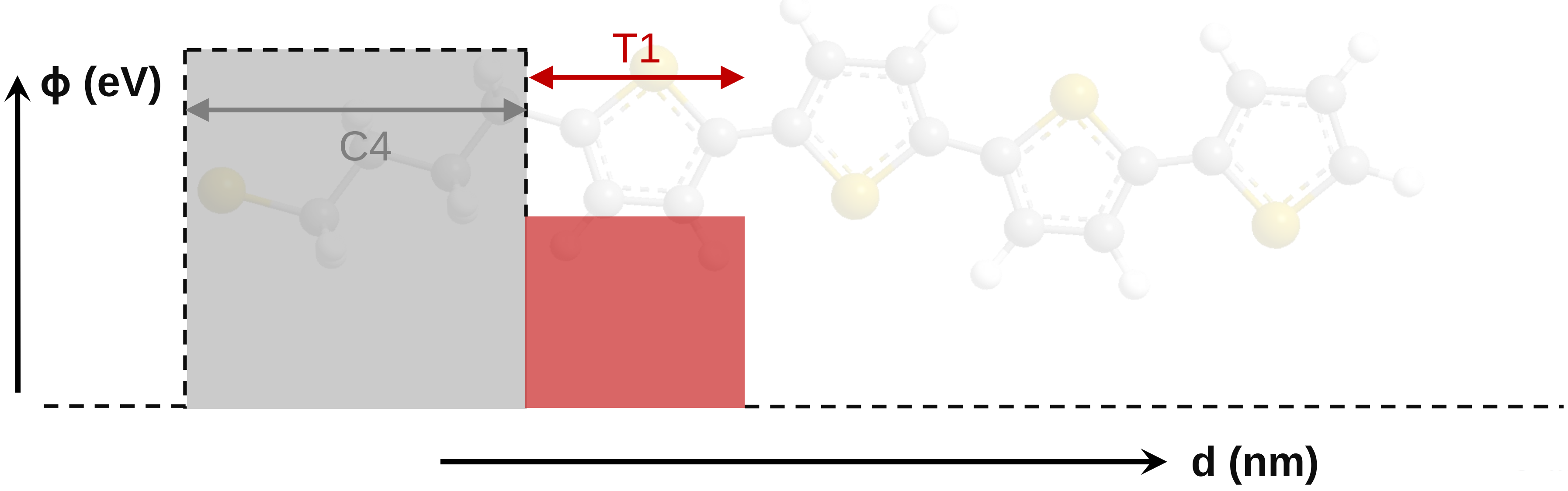
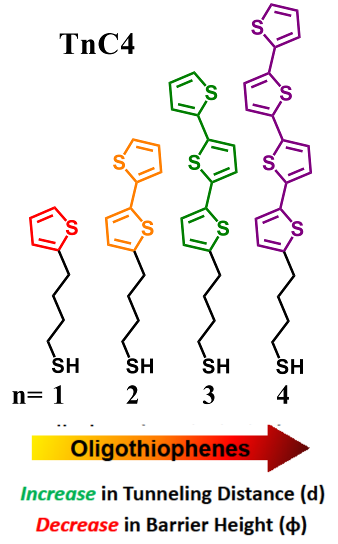
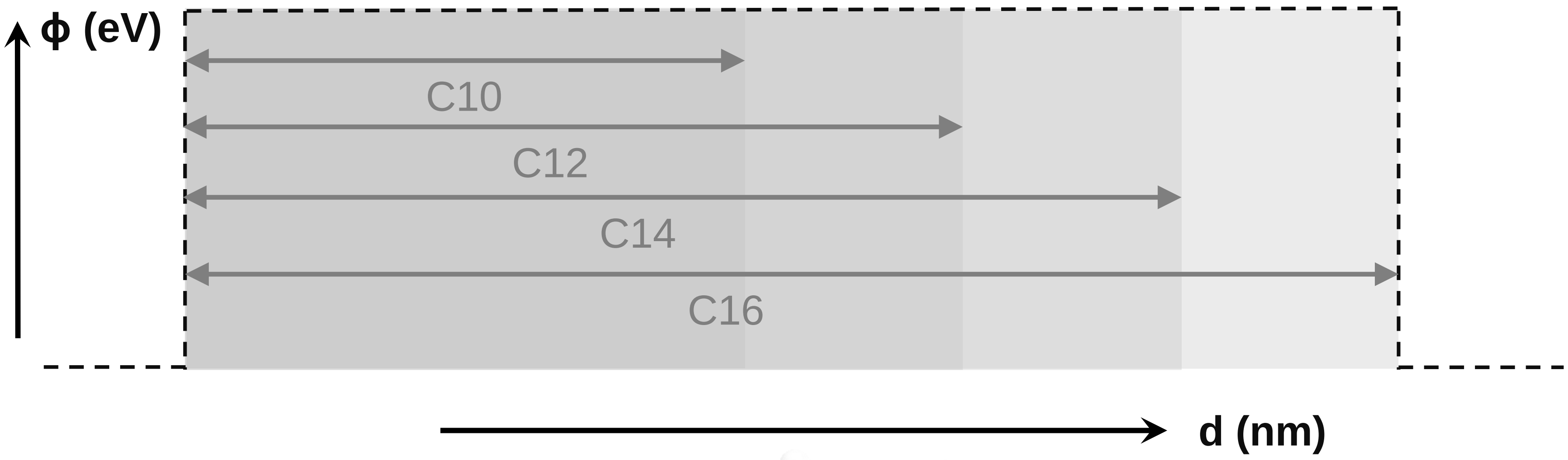


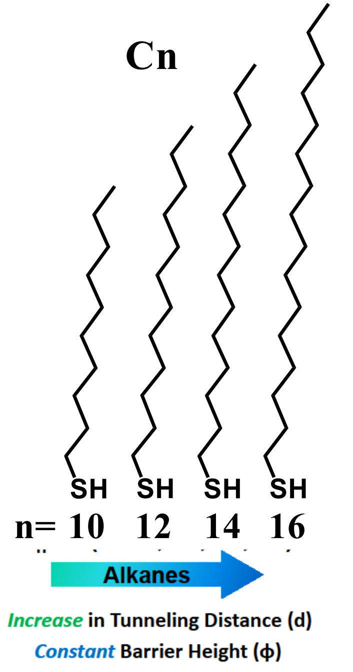


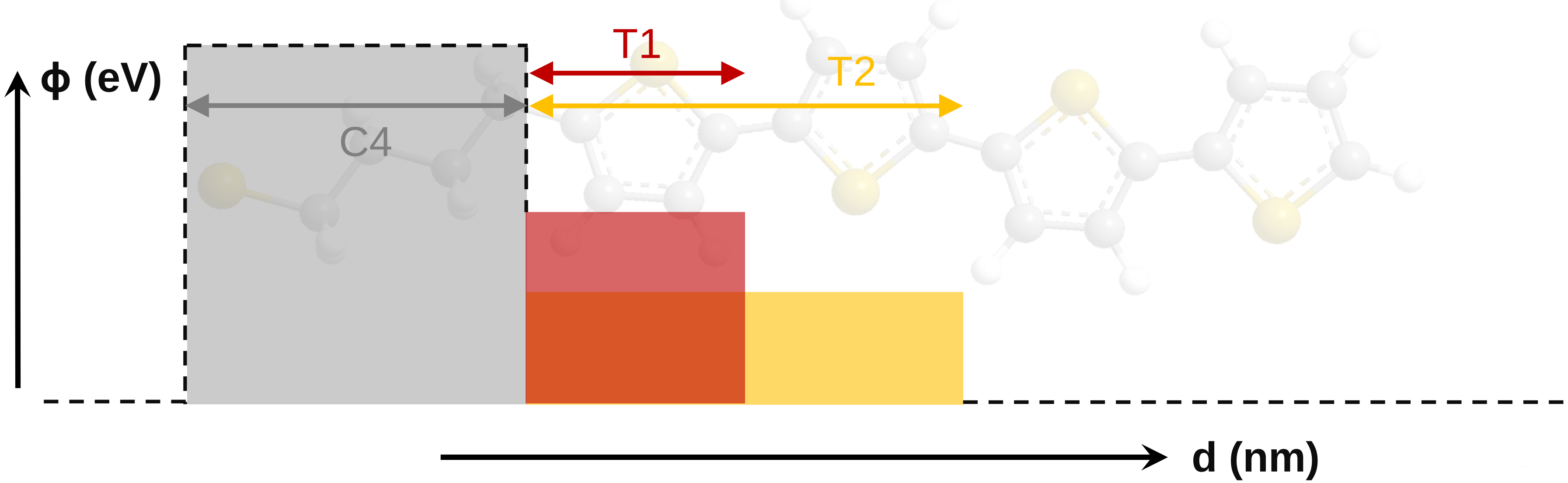


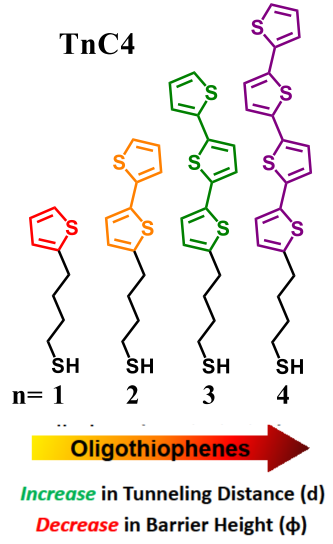


Shape of potential barriers

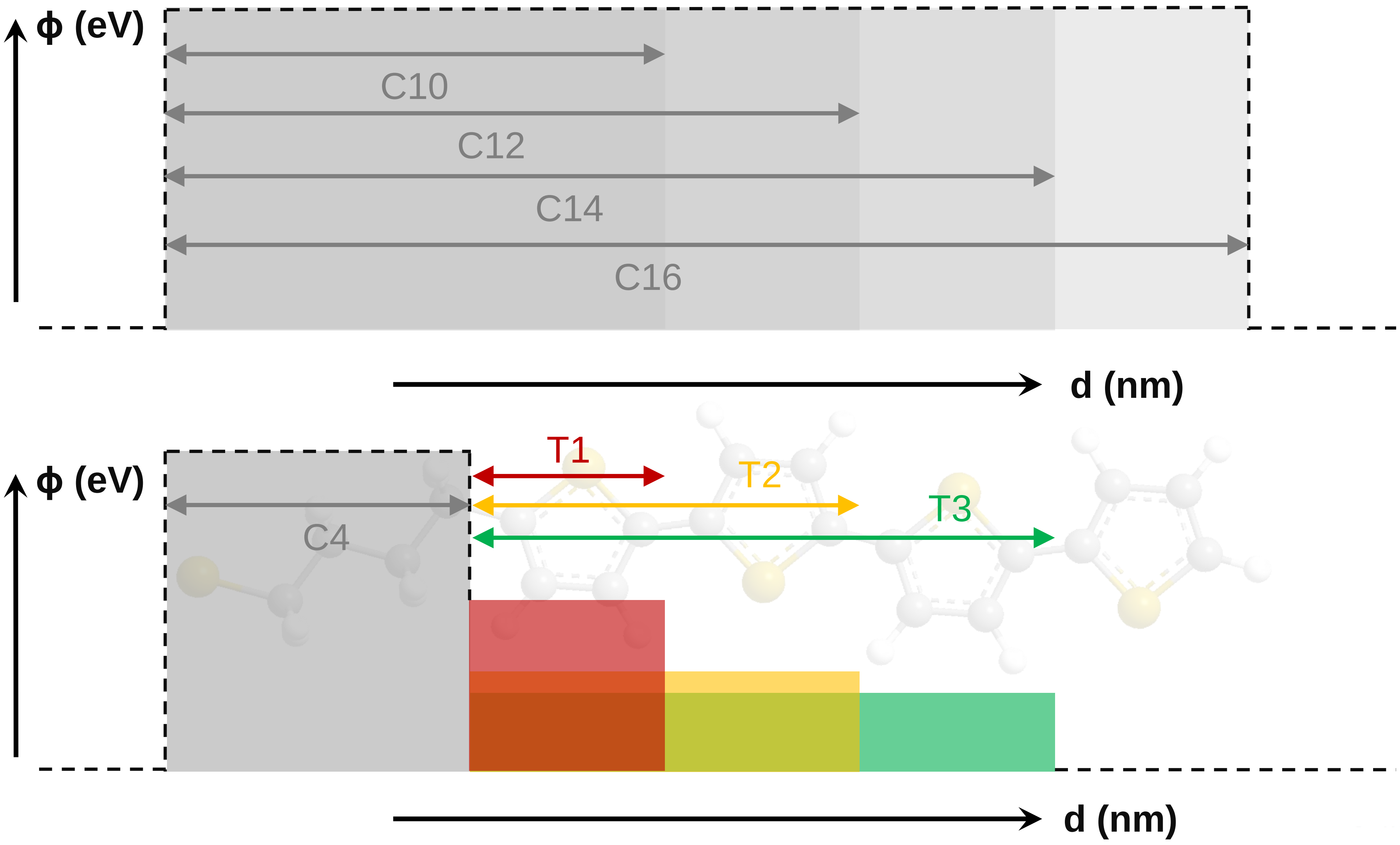


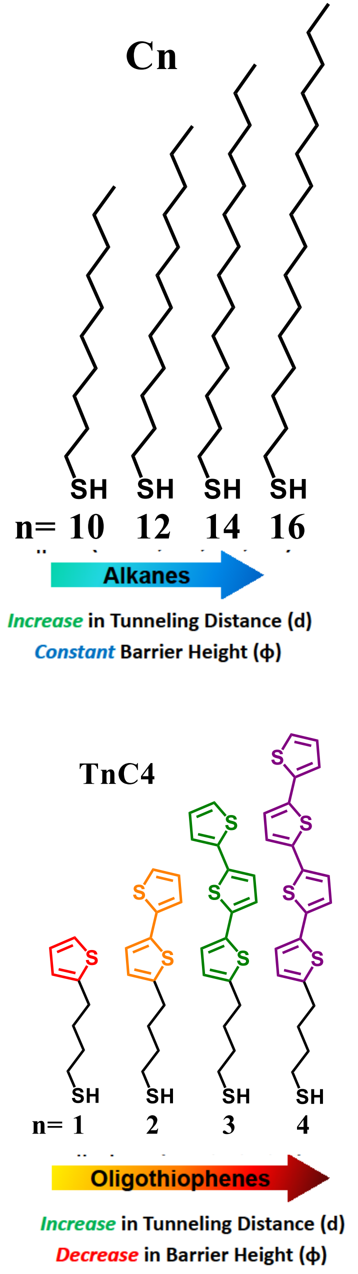




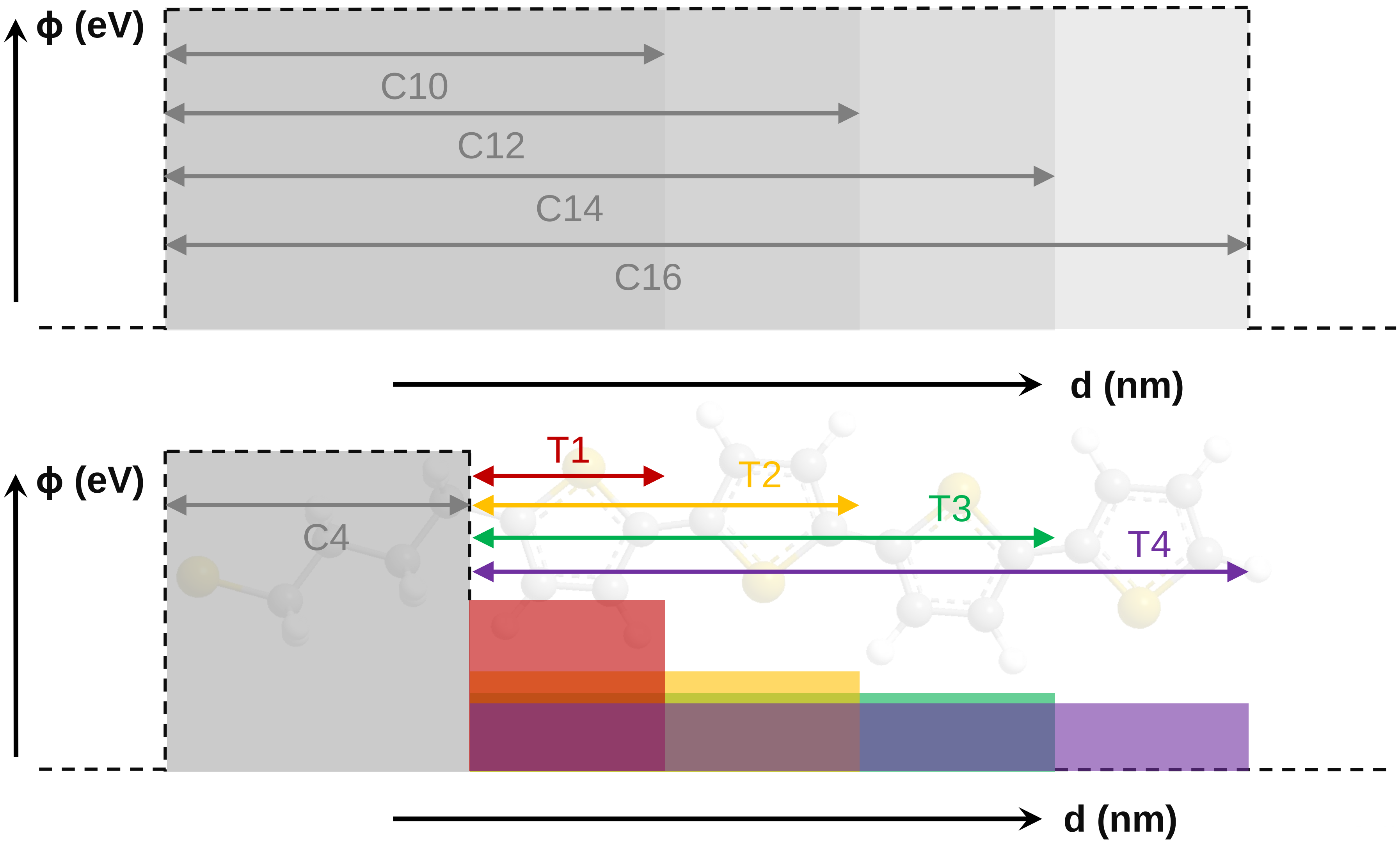


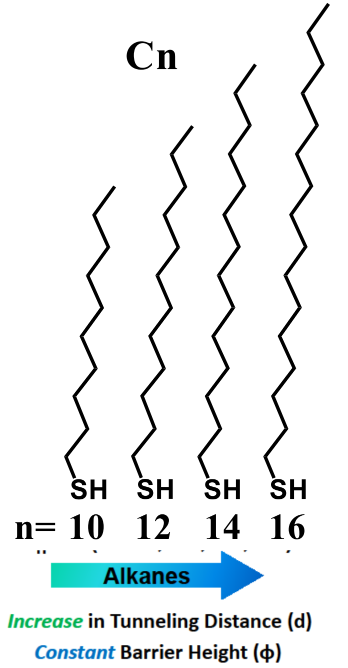
Shape of potential barriers

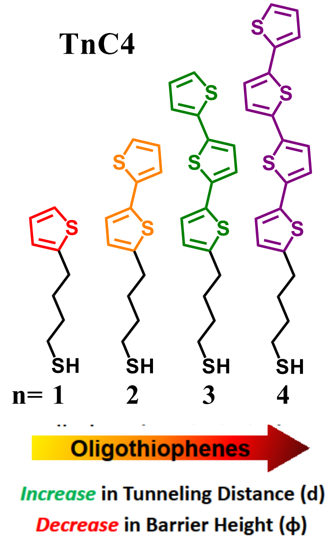




Shape of potential barriers

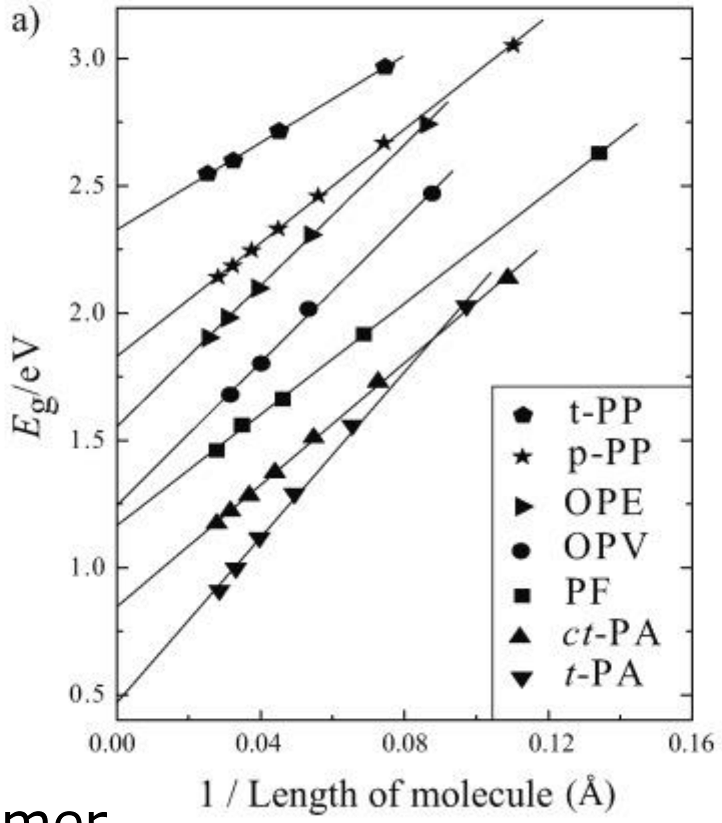






Known dependence of bandgap on molecular length

$$E_g(d) = \Delta^\infty + \frac{\alpha}{d}$$

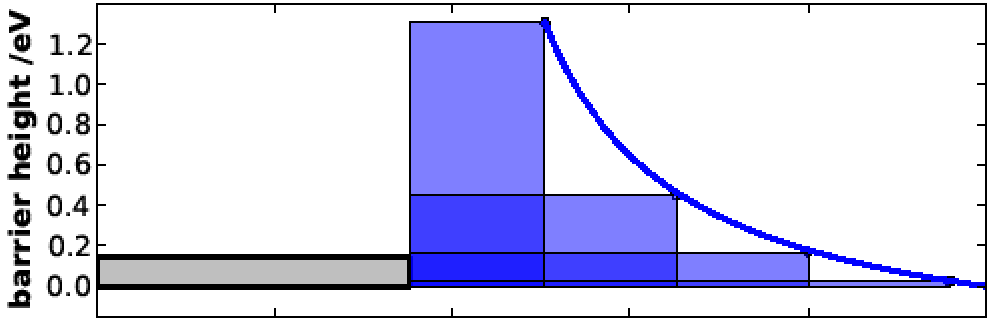


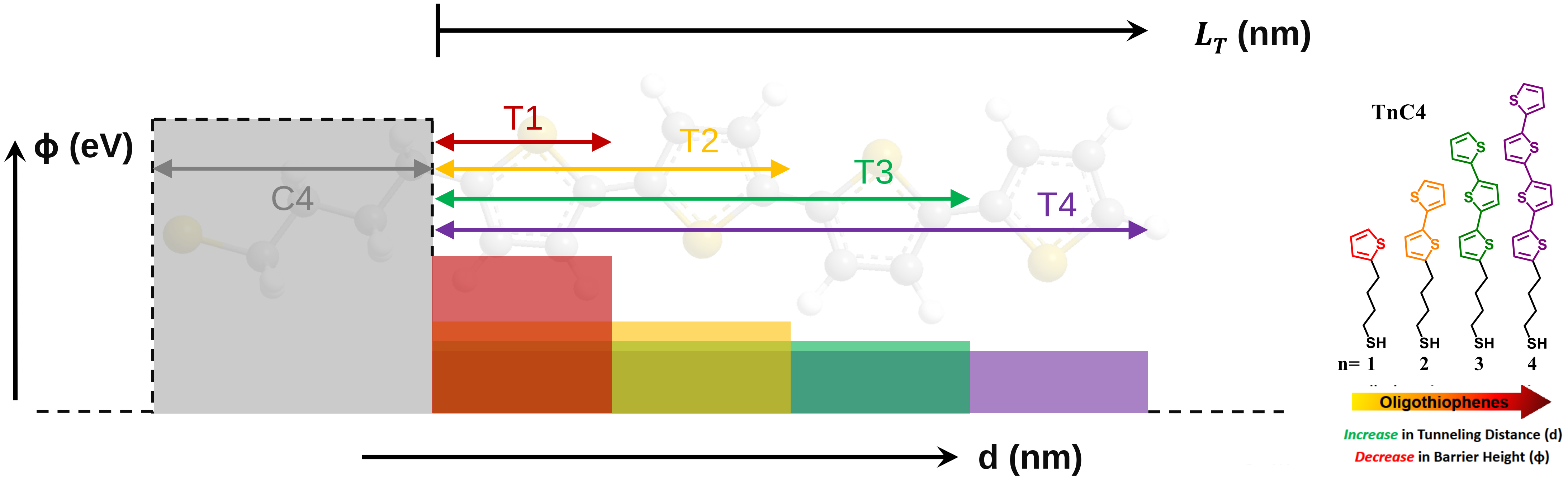
› Δ^∞ would be the value of bandgap of an infinite polymer

ChemPhysChem 2008, 9, 1416 – 1424

Shape of potential barriers

$$\phi(L_T) = \Delta^{\infty} + \frac{\alpha}{L_T}$$





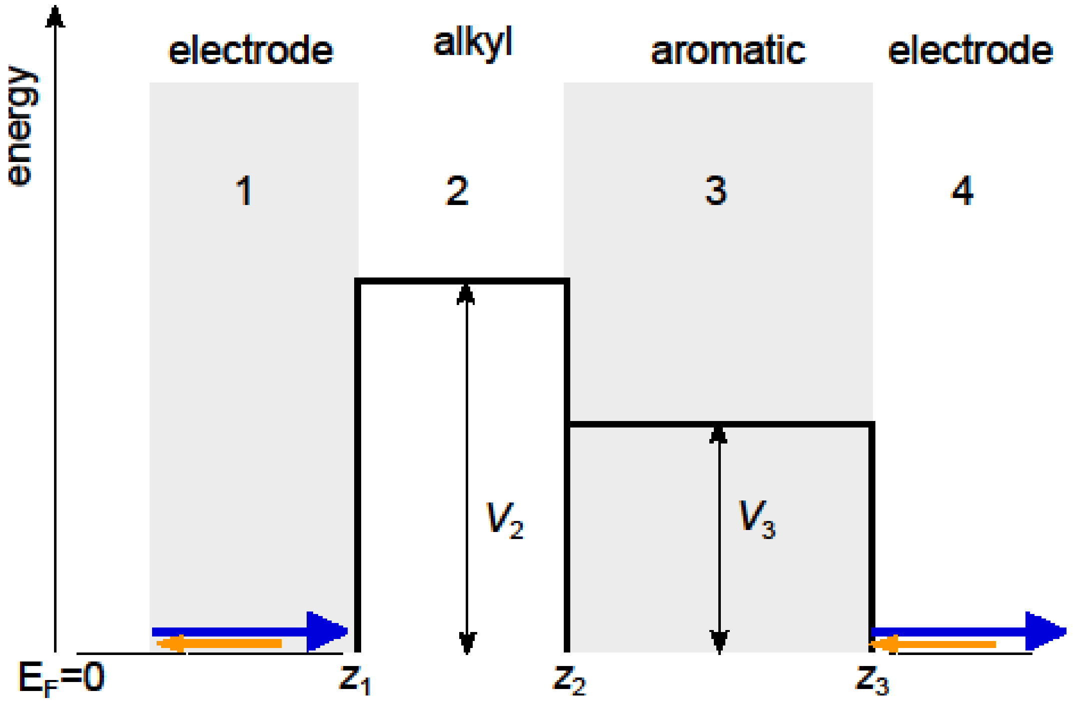
Solving 2-Barrier Model

$$\psi_p(z) = A_p e^{ik_p z} + B_p e^{-ik_p z} \qquad (z_{p-1} < z < z_p).$$

$$k_p = \sqrt{\frac{2me}{\hbar^2}(E - Vp)}$$

$$\psi_p(z_p) = \psi_{p+1}(z_p), \qquad \text{and} \qquad \frac{d\psi_p(z_p)}{dz} = \frac{d\psi_{p+1}(z_p)}{dz}.$$

$$V_3(L_T) = \Delta^{\infty} + \frac{\alpha}{L_T}$$



Calculating transmission:

$$T(E) = \frac{J_{4,\,trans}}{J_1} = \frac{|A_4|^2}{|A_1|^2}$$

Calculating transmission:

$$V_3(L_T) = \Delta^{\infty} + \frac{\alpha}{L_T}$$

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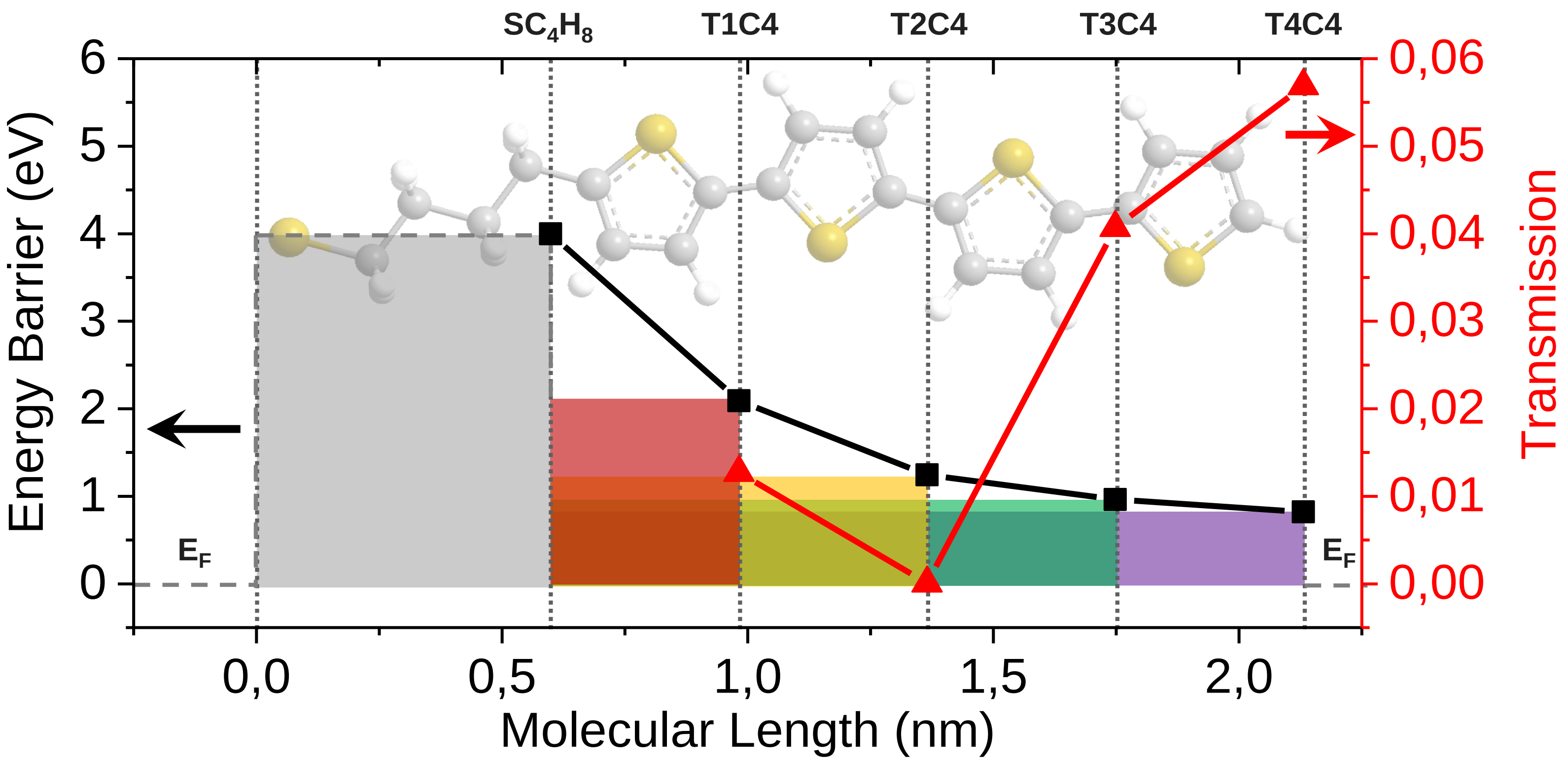
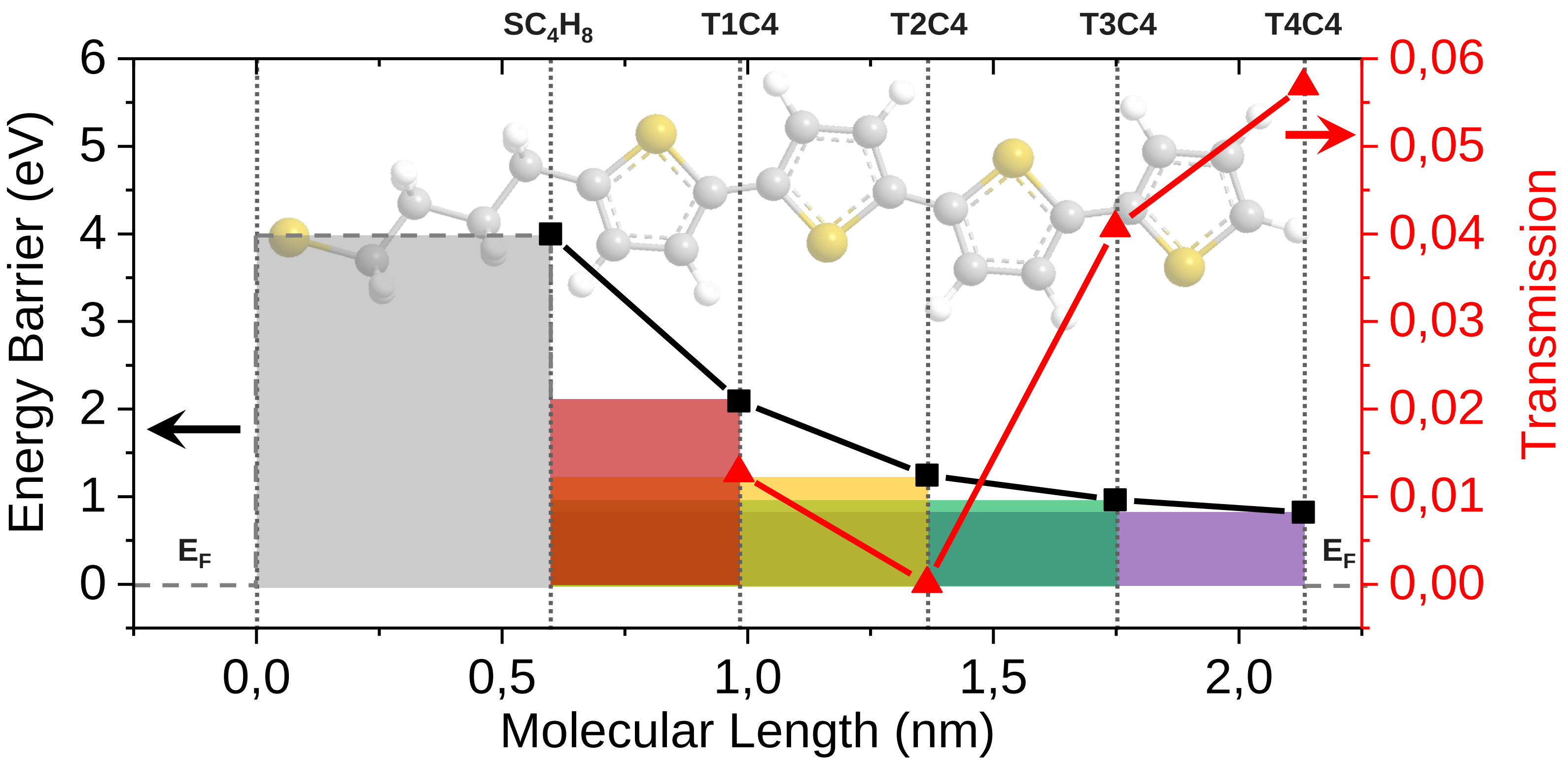


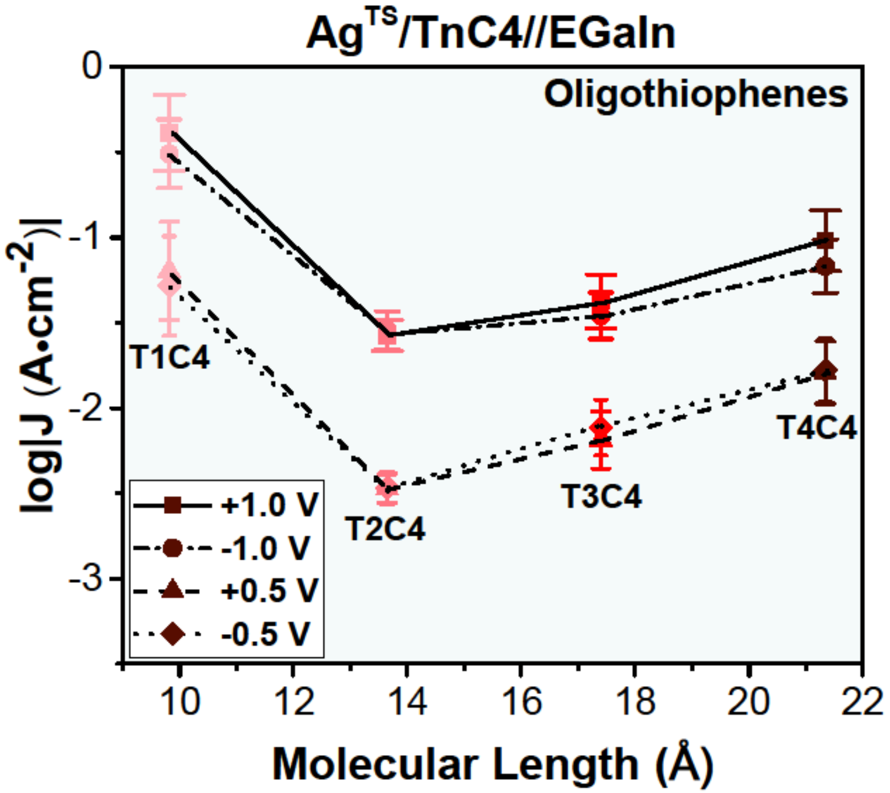
Solving 2-Barrier Model

Calculating transmission:

- The exact curvature and the trend depends on the values of parameters $\boldsymbol{\Delta}^{\infty}$ and $\boldsymbol{\alpha}$.

$$V_3(L_T) = \Delta^{\infty} + \frac{\alpha}{L_T} \qquad T(E) = \frac{J_{4\,trans}}{J_1} = \frac{|A_4|^2}{|A_1|^2}$$



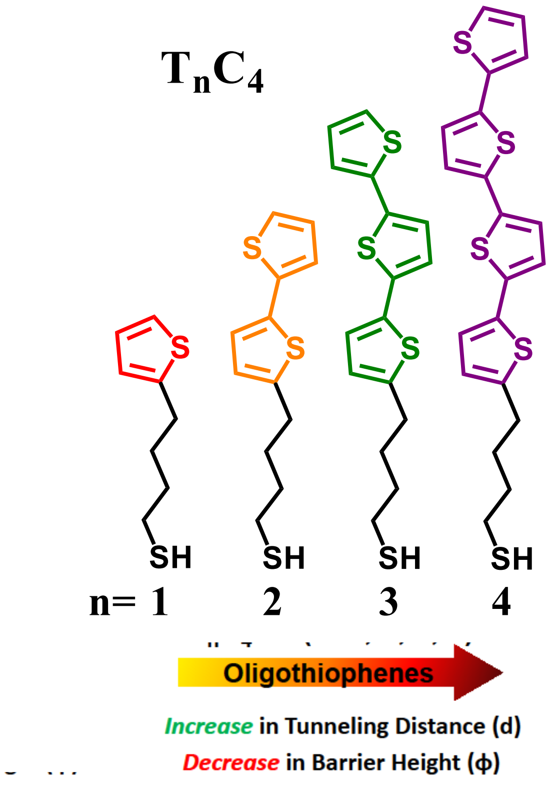


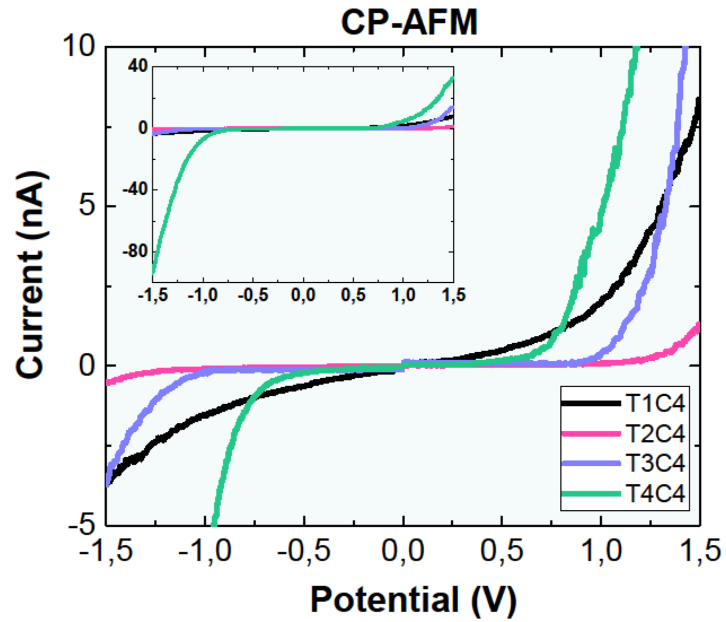
I-V and NDC Simulations

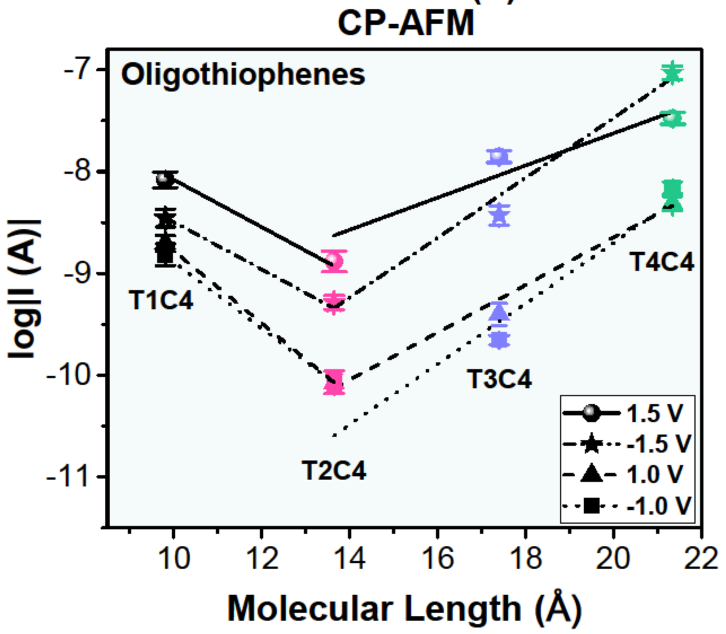
1) Simulating CP AFM *I-V* curves (DFT)

Experimental….

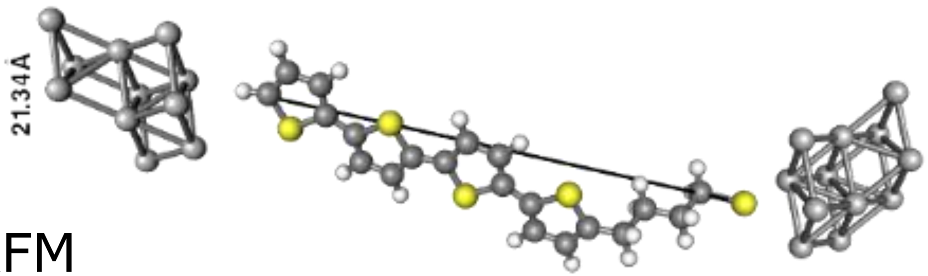
- $T_4C_4 > (T_3C_4 \sim T_1C_4) > T_2C_4$







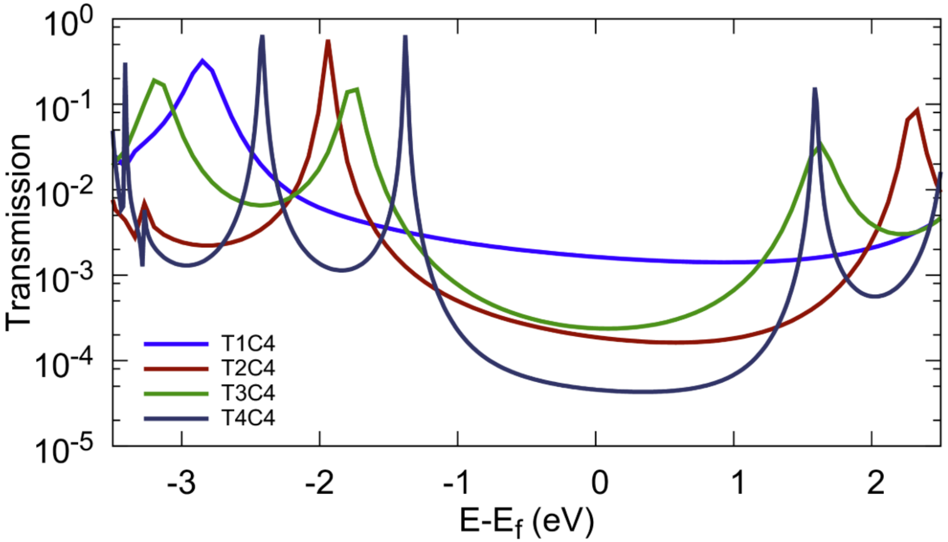
1) Simulating CP AFM *I-V* curves (DFT)



- Single-molecular DFT calculations closer to CP AFM
- Input: T(E) from DFT on single-molecular junctions

$$I(V) = \frac{2e}{h} c \int_{E_F - eV/2}^{E_F + eV/2} T(E).dE$$

(Chem. Soc. Rev.2015,44, 875–888)



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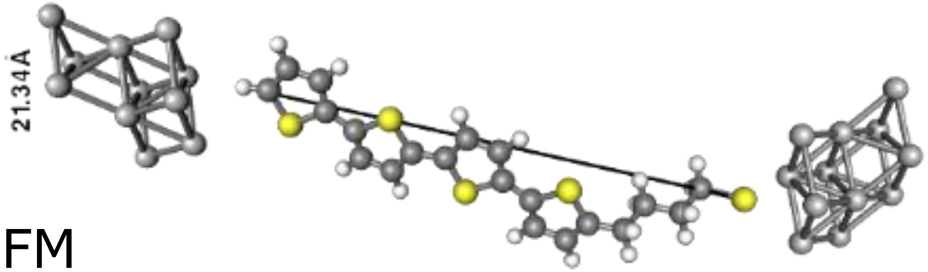

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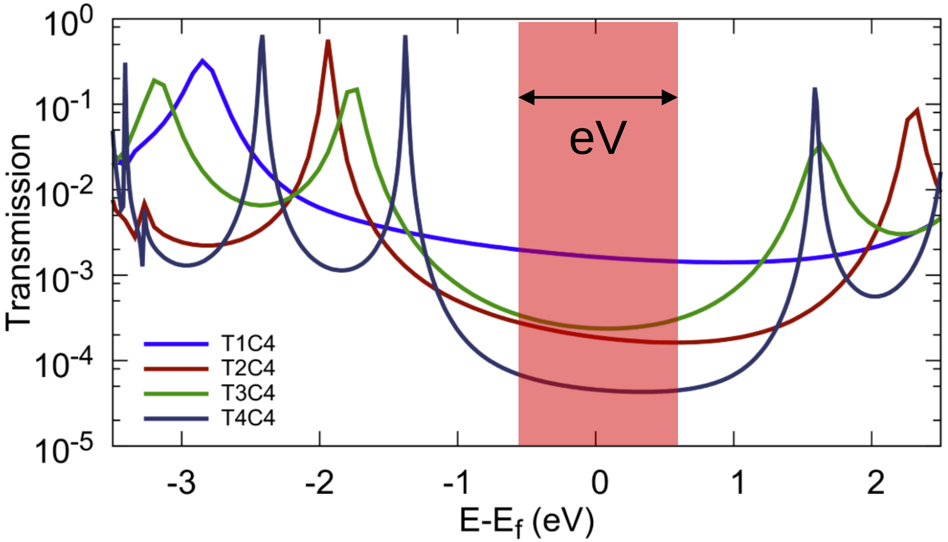
(Chem. Soc. Rev.2015,44, 875–888)

- Integrating the area under the curve for an energy range of eV for every value of V



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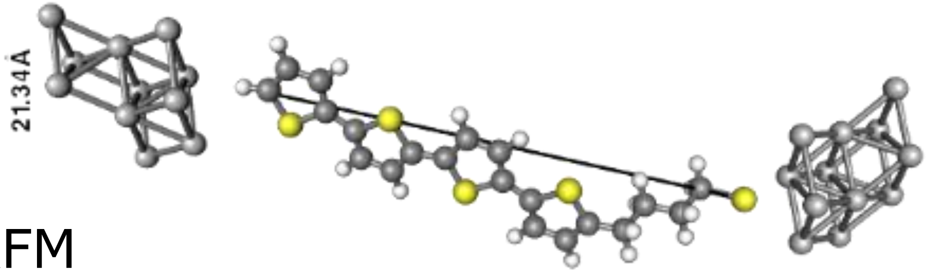

- Single-molecular DFT calculations closer to CP AFM
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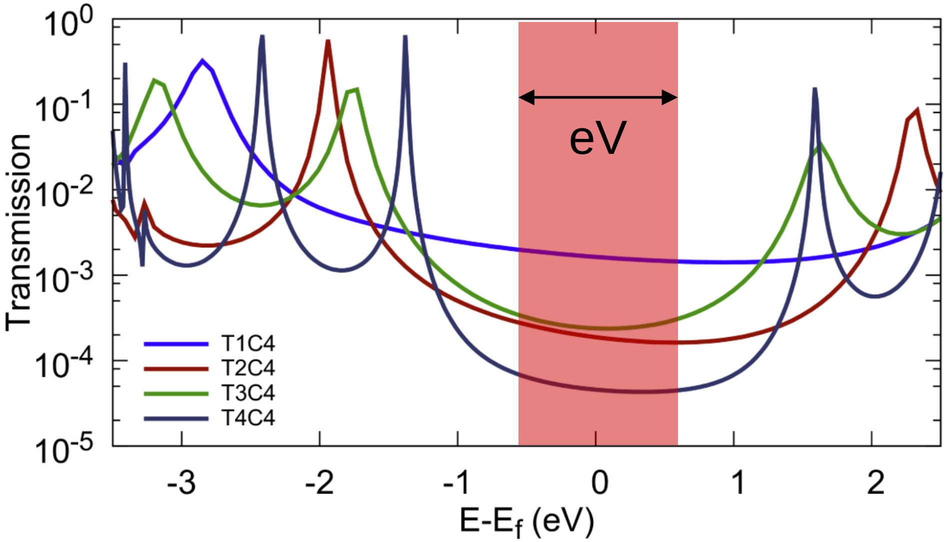
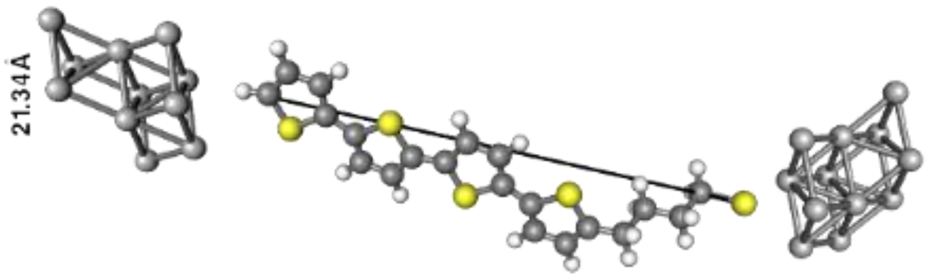
$$I(V) = \frac{2e}{h} c \int_{E_F - eV/2}^{E_F + eV/2} T(E).\, dE$$

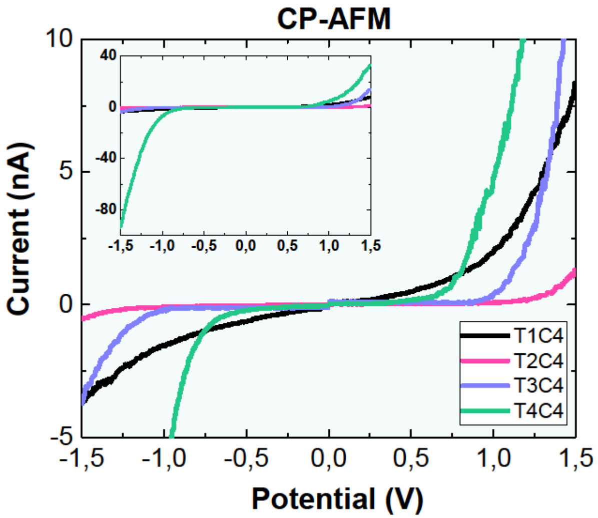
(Chem. Soc. Rev.2015,44, 875–888)

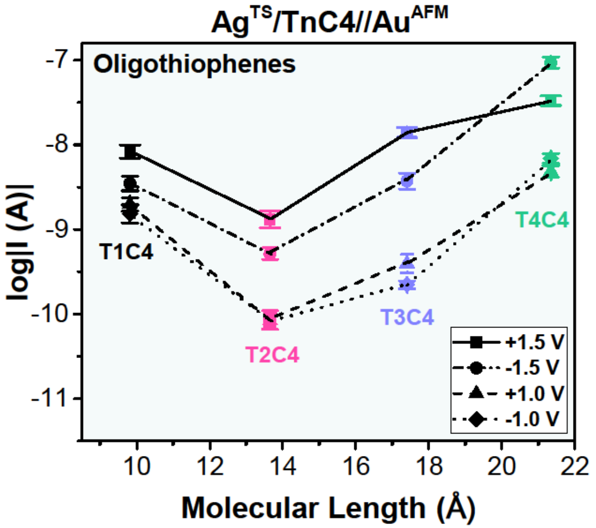
- Integrating the area under the curve for an energy range of eV for every value of V
  - Ef = -4.7eV
  - T(E) already contains molecules' DOS
  - Small constant (0.0001) added to T(E)

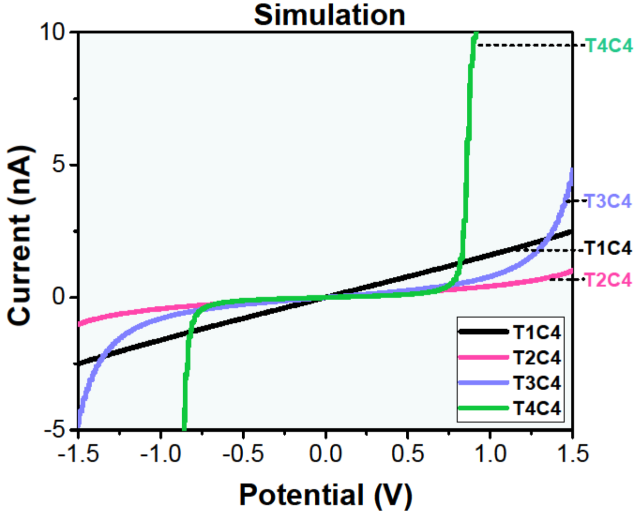


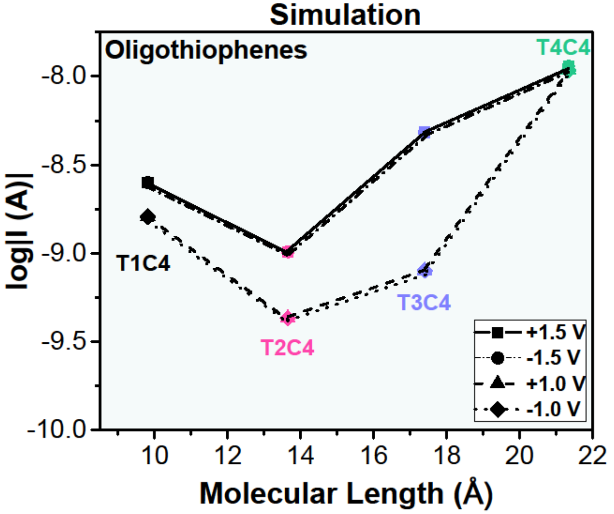
1) Simulating CP AFM *I-V* curves (DFT)



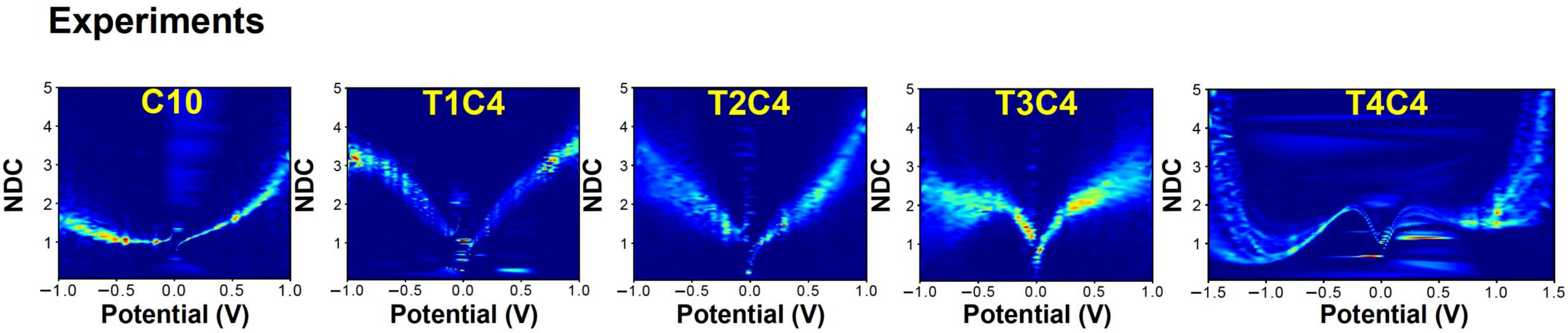








2) Simulating Normalised Differential Conductance (NDC)



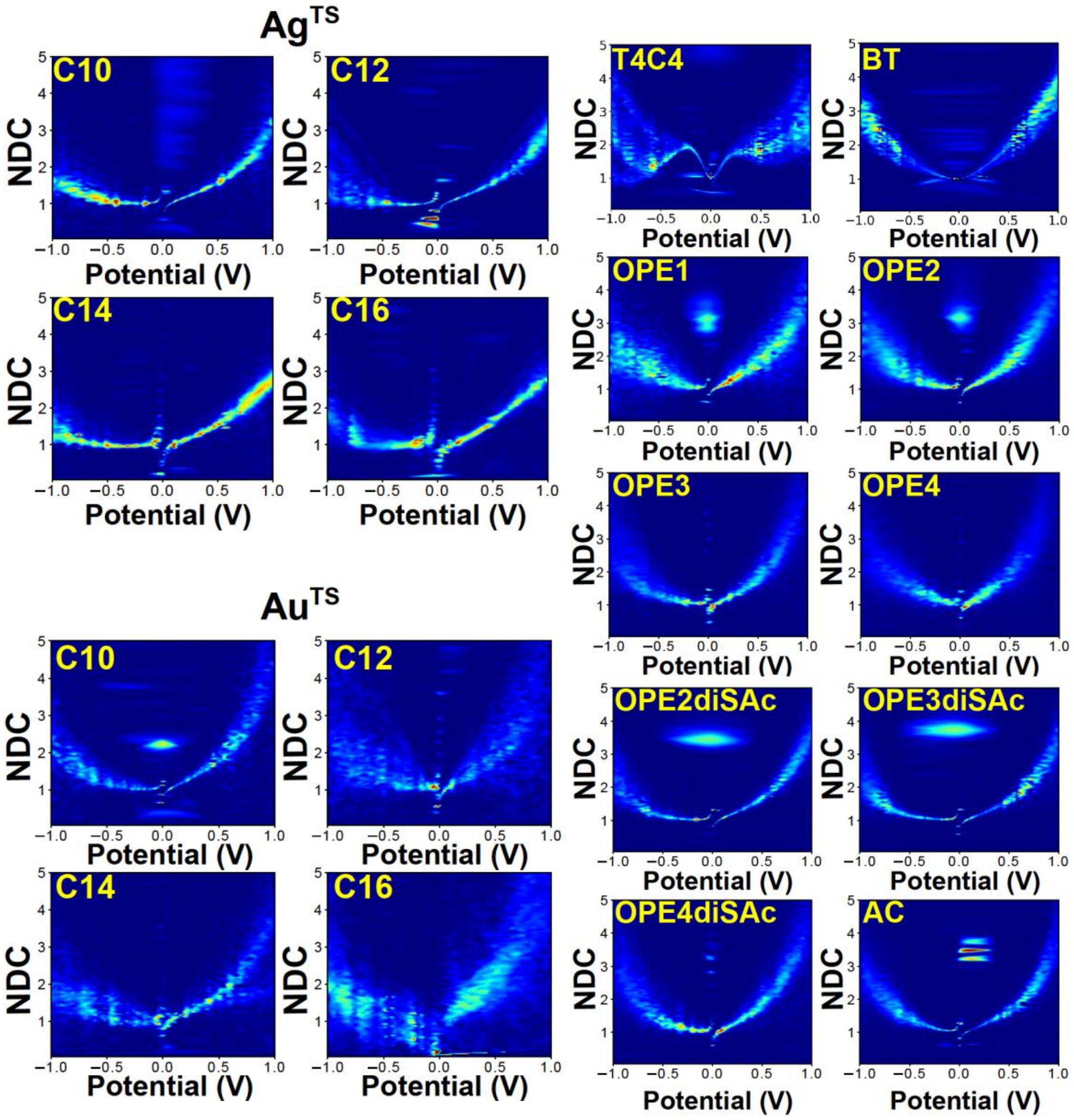
NDC = (dI/dV)/(I/V)

- EGaIn measurements show bumps closing-in in the NDC curves as we go from T_1C_4 to T_4C_4

2) Simulating Normalised Differential Conductance (NDC)

NDC = (dI/dV)/(I/V)

› EGaIn NDC curves for aliphatic and conjugated molecules, otherwise do not show any bumps



2) Simulating Normalised Differential Conductance (NDC)

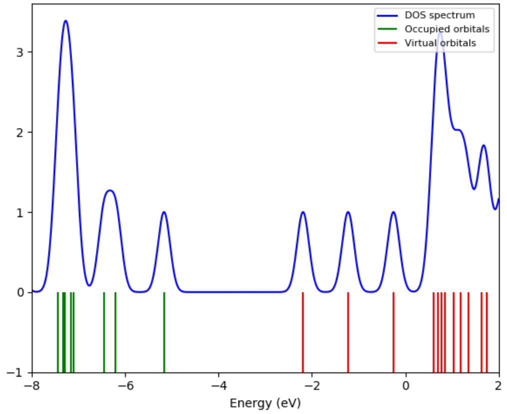
NDC = (dI/dV)/(I/V)

- **Input:** DOS from DFT
  DOS: Gaussian Fits to discrete energy levels of gas-phase single molecules

- **Input:** T(E) from STM equation

$$T(E, eV) = e^{-2d\sqrt{\frac{2m}{\hbar^2}\left(\phi - E + \frac{eV}{2}\right)}}$$

d is barrier width, $\boldsymbol{\phi}$ is work function



2) Simulating Normalised Differential Conductance (NDC)

$$I(V) = c\int_{E_F - eV/2}^{E_F + eV/2} T(E, eV).DOS(E).dE$$

- Integrating the area under the curve for an energy range of eV for every value of V

2) Simulating Normalised Differential Conductance (NDC)

$$I(V) = c\int_{E_F - eV/2}^{E_F + eV/2} T(E, eV).\,DOS(E).\,dE$$

- Integrating the area under the curve for an energy range of eV for every value of V
  - Ef = -4.7 eV
  - Small constant (0.005) added to DOS(E), so that it is not zero anywhere
  - Tunnelling barrier only comprises of the alkyl part

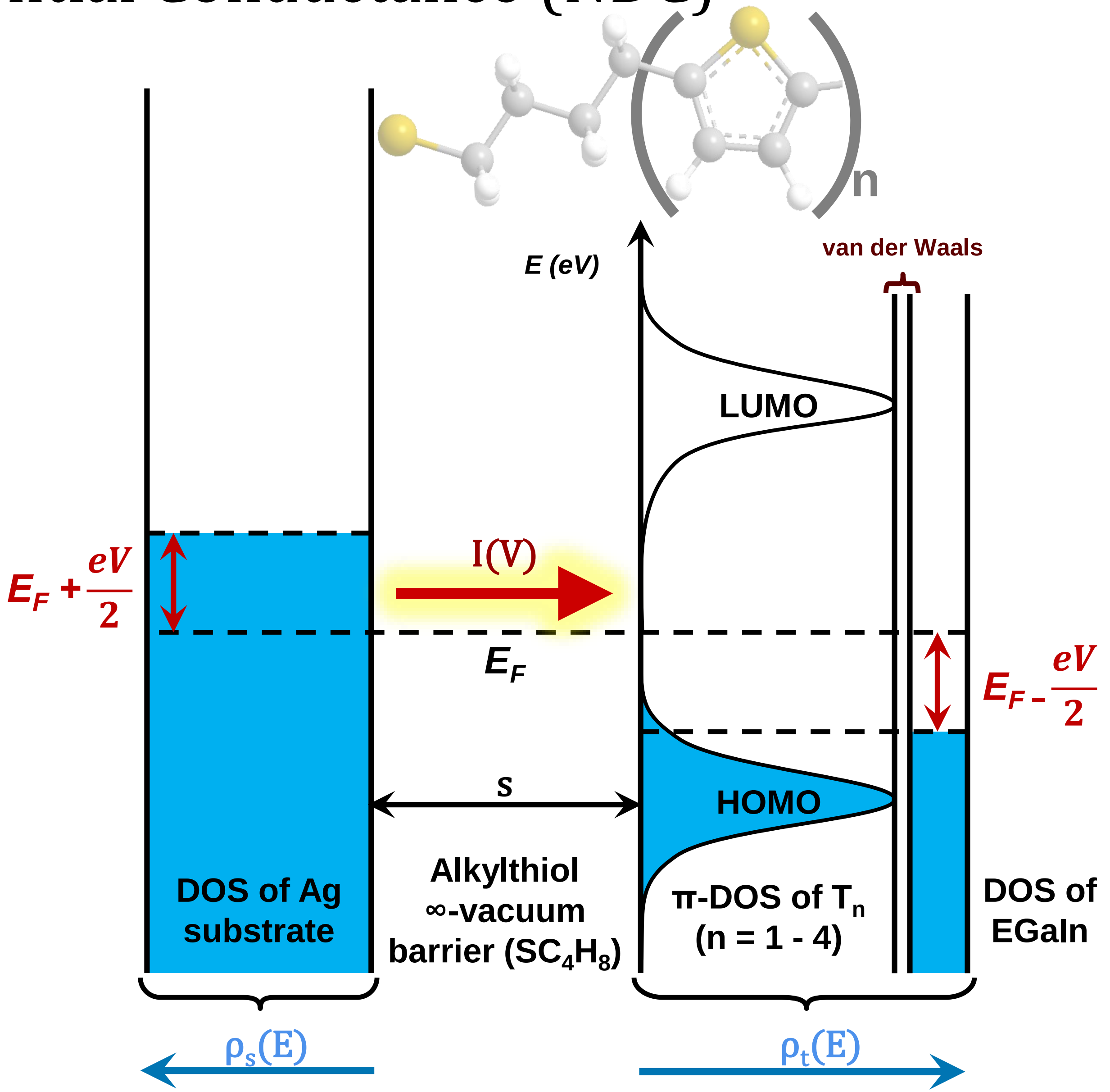
NDC = (dI/dV)/(I/V)

2) Simulating Normalised Differential Conductance (NDC)

Input 1: *DOS(E)* from DFT Gaussian fits

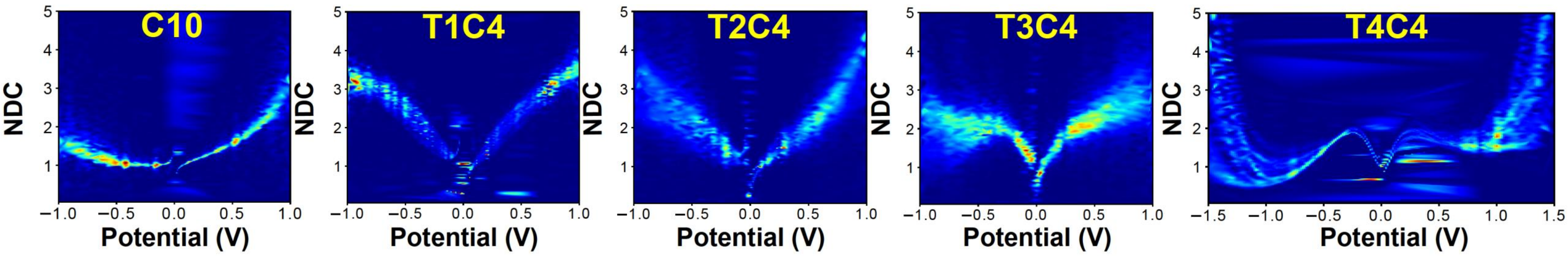
Input 2: $T(E, eV) = e^{-2d\sqrt{\frac{2m}{\hbar^2}\left(\phi - E + \frac{eV}{2}\right)}}$

$$I(V) = c\int_{E_F - eV/2}^{E_F + eV/2} T(E, eV).DOS(E).dE$$

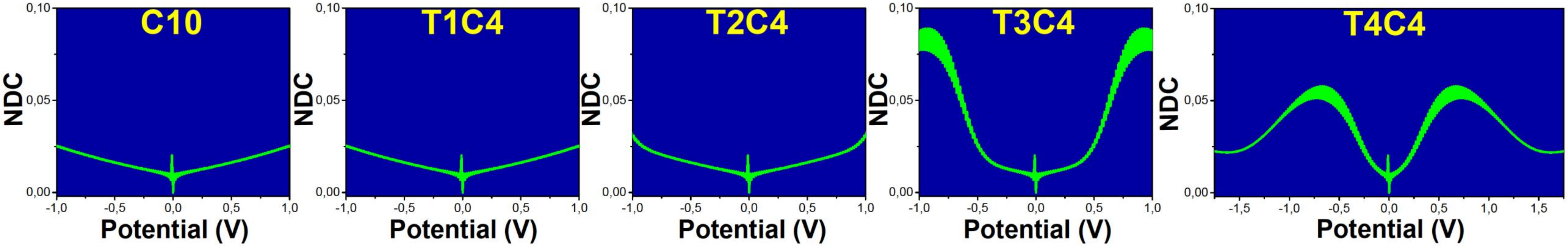


2) Simulating Normalised Differential Conductance (NDC)

A) Experiments



B) Simulations



Thank you for your attention!

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Article

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Tunneling Probability Increases with Distance in Junctions Comprising Self-Assembled Monolayers of Oligothiophenes

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