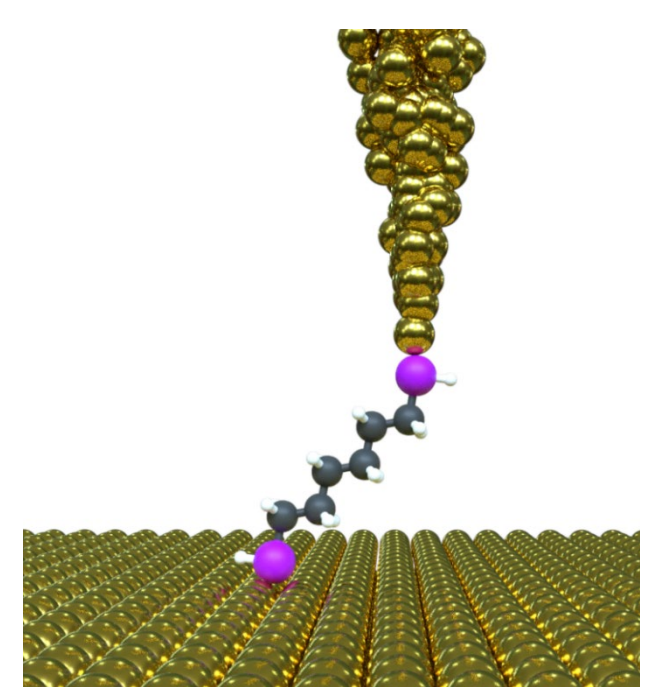


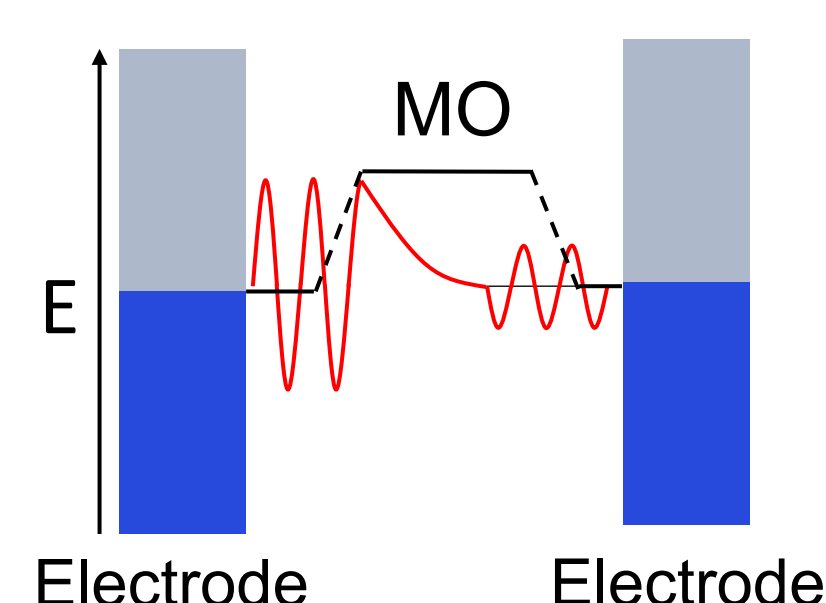
## Introduction

The ability to reliably form molecular junctions now allows measurement of the electrical conductance of single molecules and rapid advancement of the field of molecular electronics. A wide variety of molecular structure-electrical property relationships have been proposed based on these measurement, from “single parameter” models relating to the strength of molecule-electrode coupling, molecular length or energy of a critical molecular orbital (MO) in the charge transport pathway, drawn from treating the molecule as a simple tunnel barrier, to more complete treatments contained in a full Landauer-Büttiker model.<sup>1,2</sup> The role of quantum interference effects arising from the passage of the transmitting electron wave through multiple energetically accessible levels in the molecule have also been identified.<sup>3,4</sup> Here we describe the design and synthesis of a range of molecules to test some of these structure-property relationships and identify the more widely applicable model.<sup>5,6</sup>

### Molecular Junction

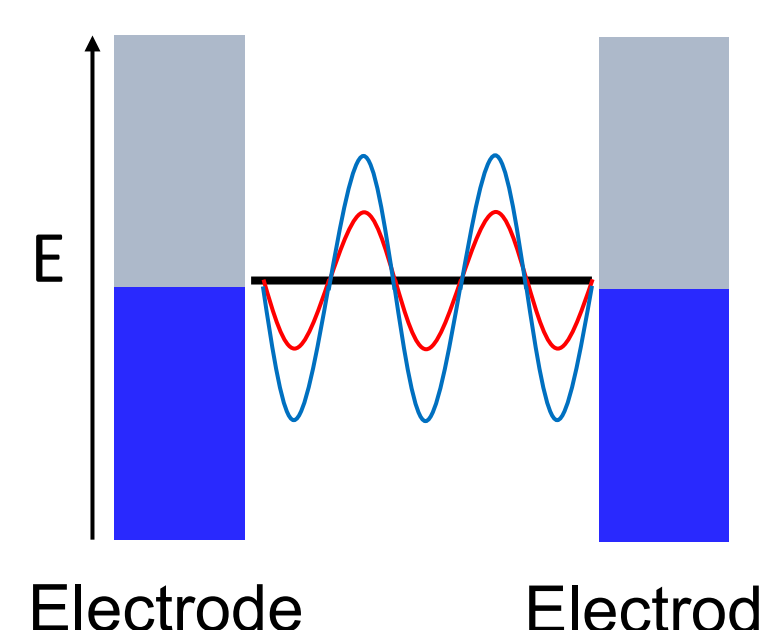


### Single channel transmission

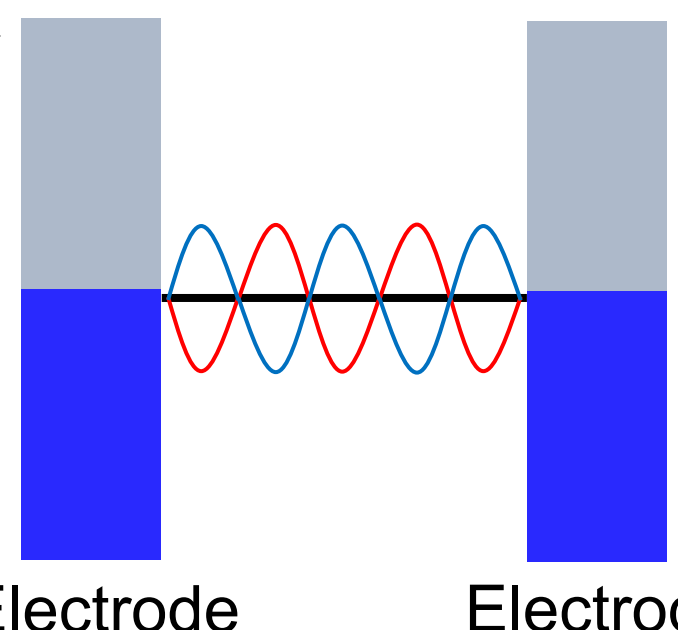
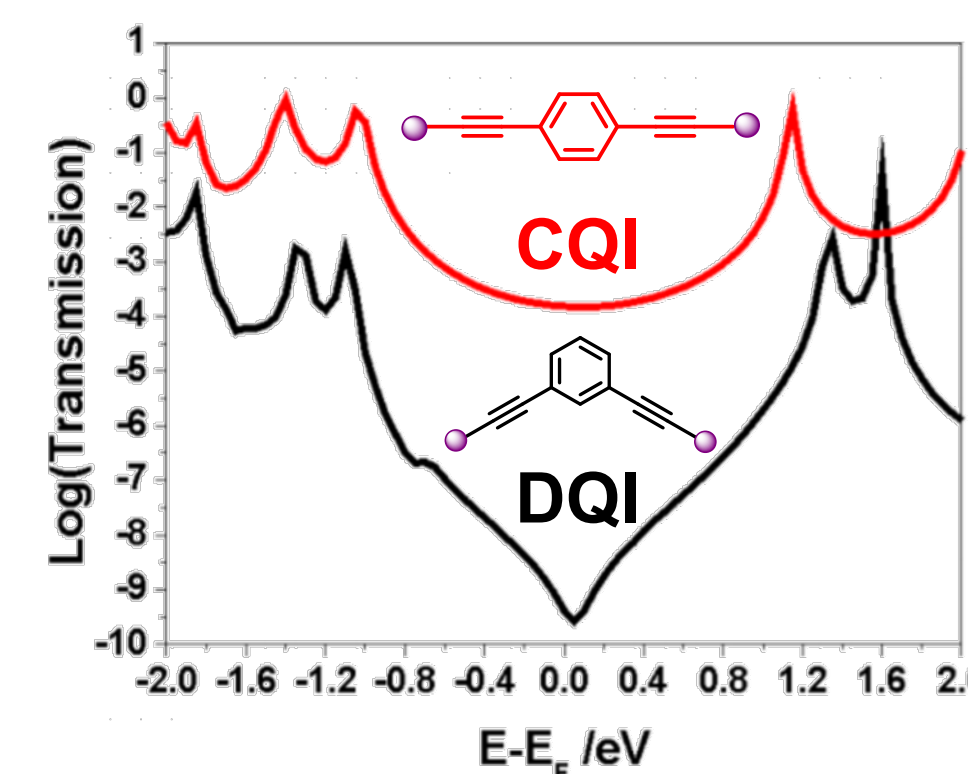


### Multiple channel transmission

#### Constructive QI (CQI)

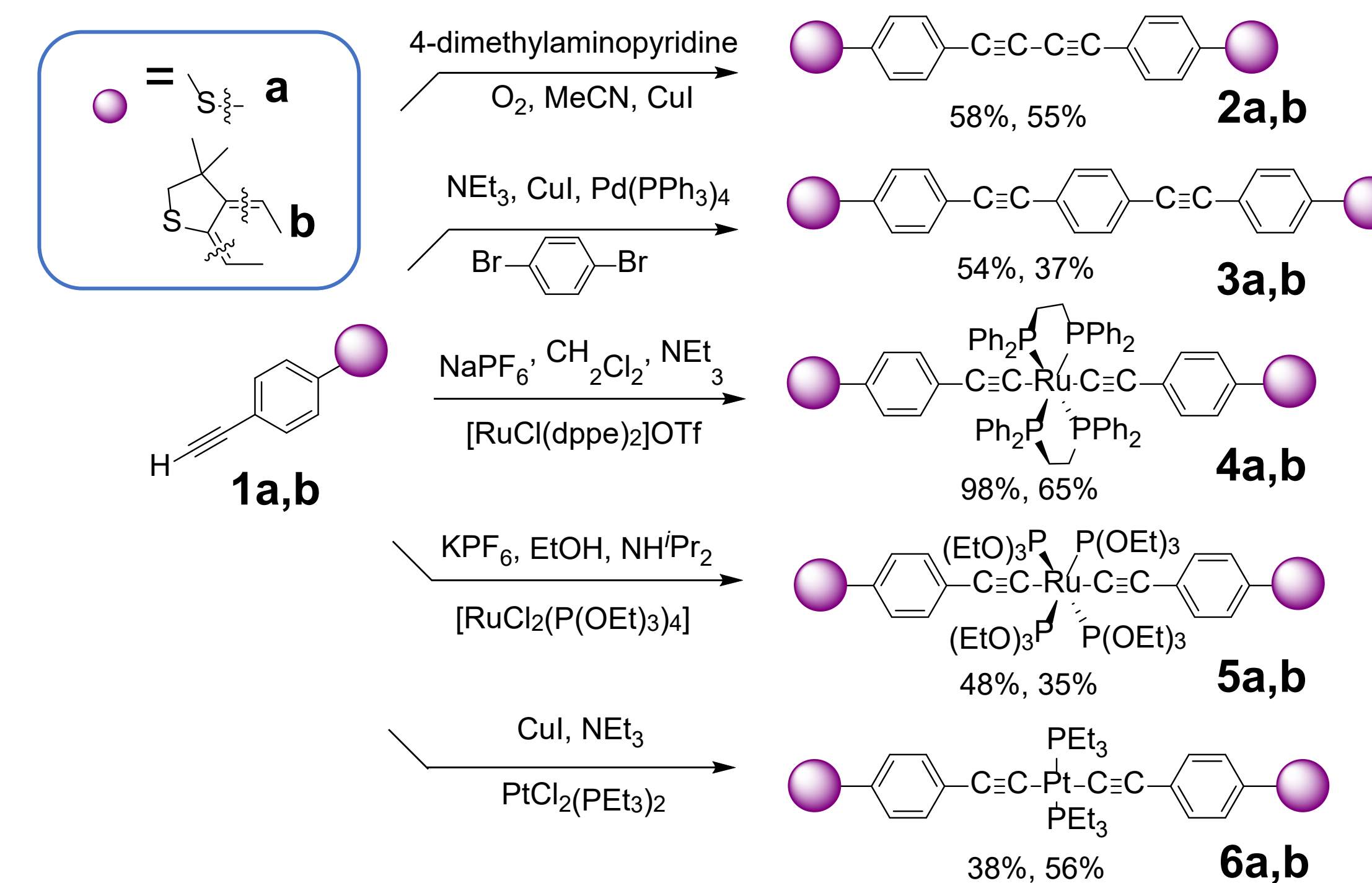
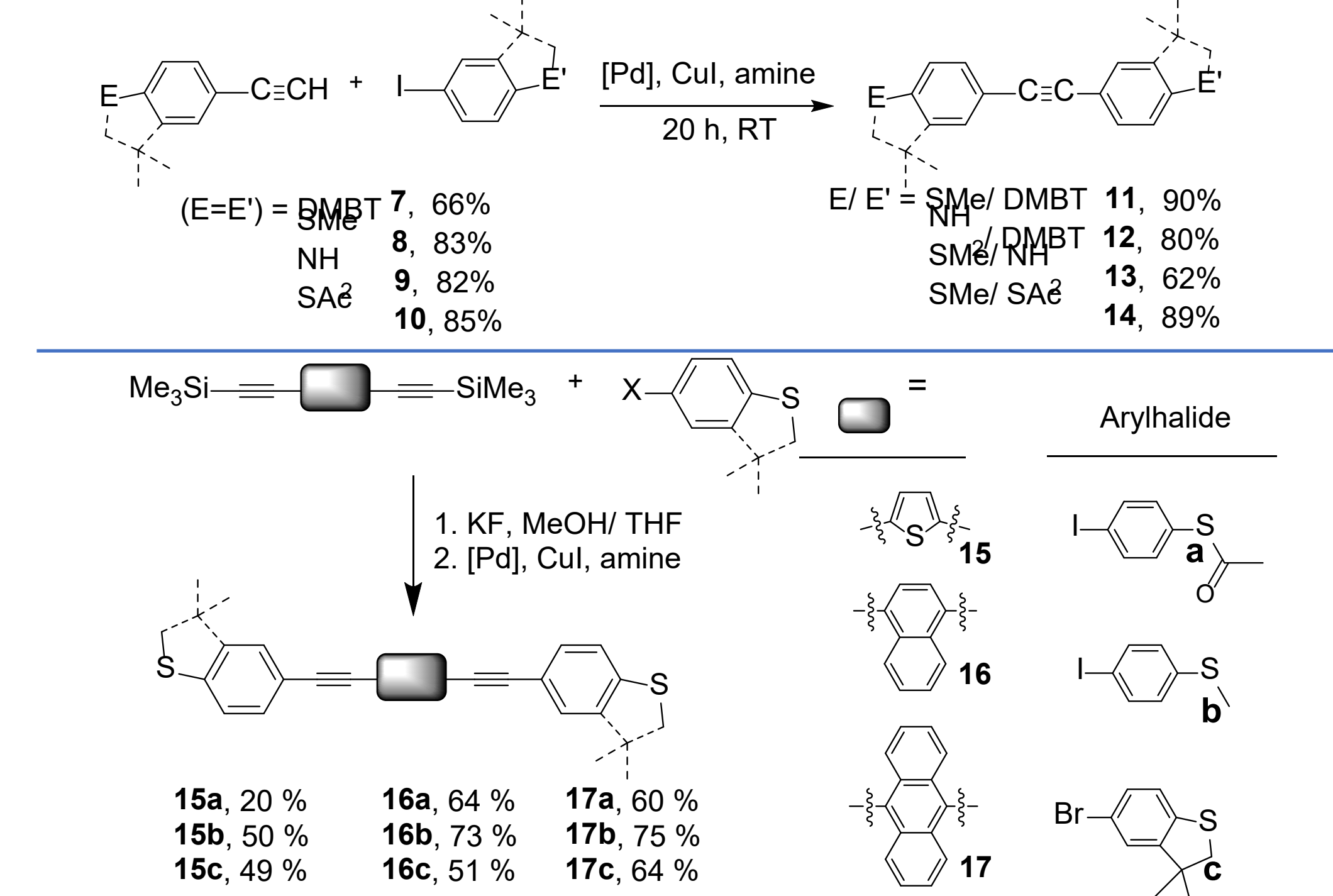


#### Destructive QI (DQI)



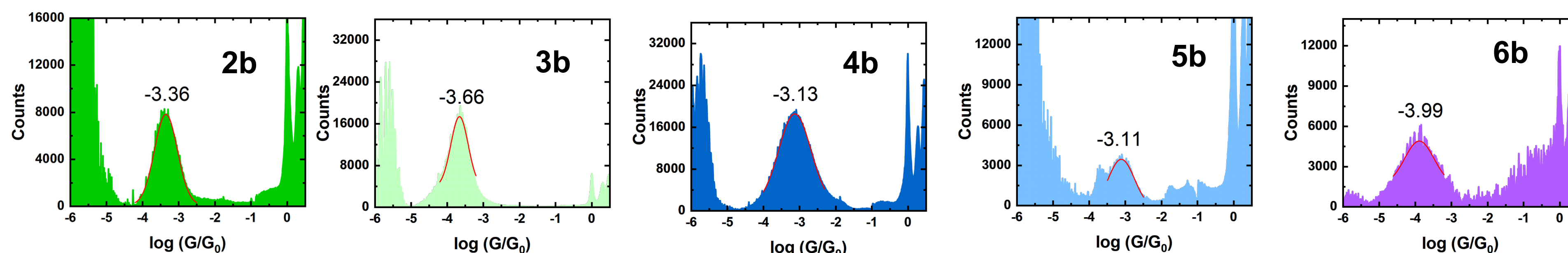
## Design and Synthesis of Molecular wires

Molecular wires are designed to offer combinations of anchor groups, molecular length, HOMO energy and “aromaticity” of the bridge in order to study molecular structure-electrical property relationships



## Modelling Molecular Conductance

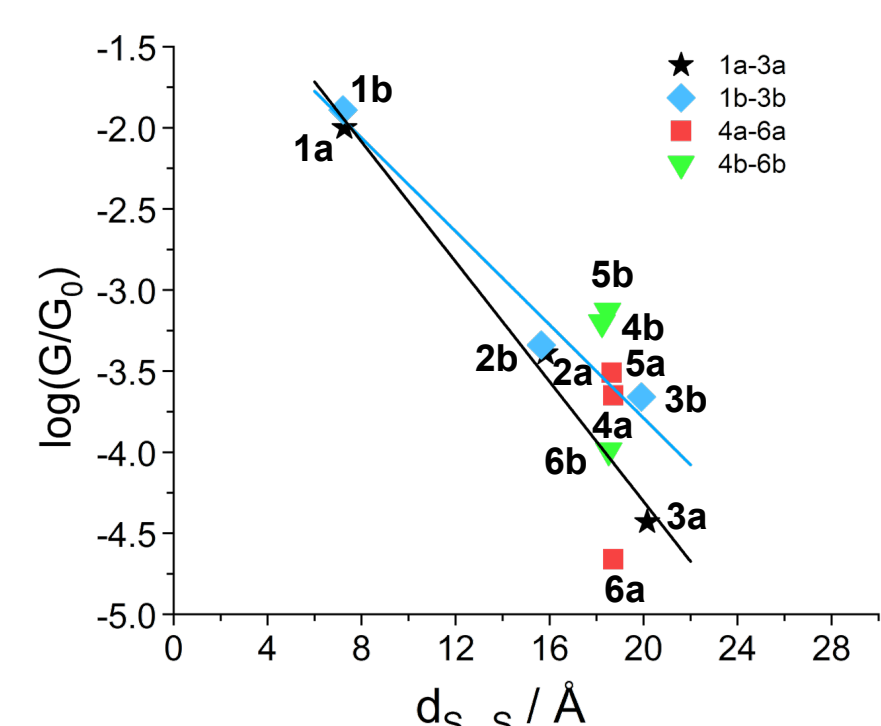
### Conductance measurement- Scanning Tunnelling Microscopy Break Junction (STM-BJ) Technique



### Correlations of Conductance with Molecular Length

$$G \propto e^{-\beta l}$$

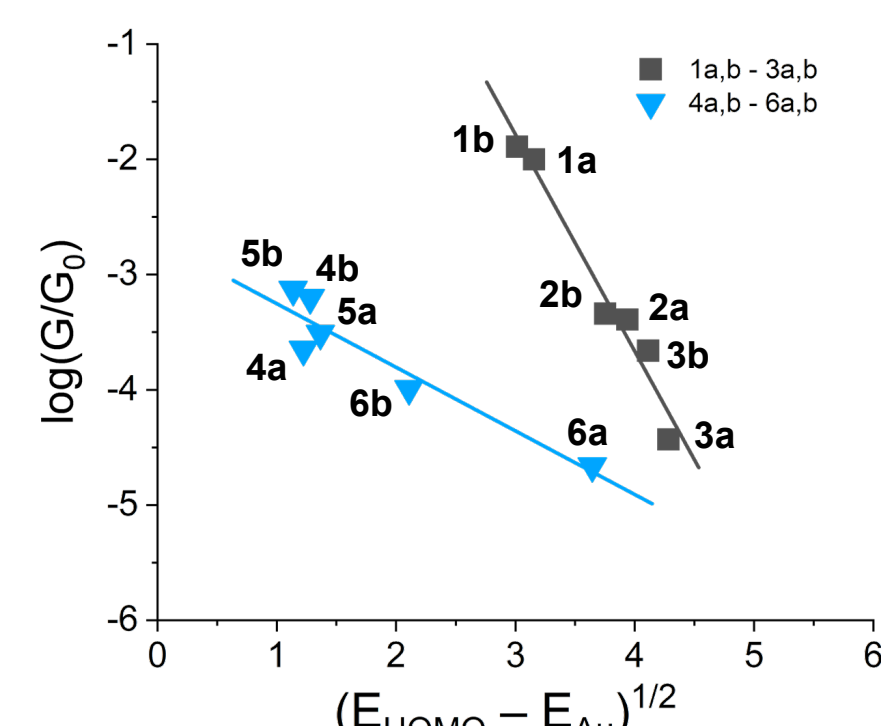
$l$  = molecular length



### Correlation of conductance with molecular orbital energies

$$G \propto e^{-\Delta E l}$$

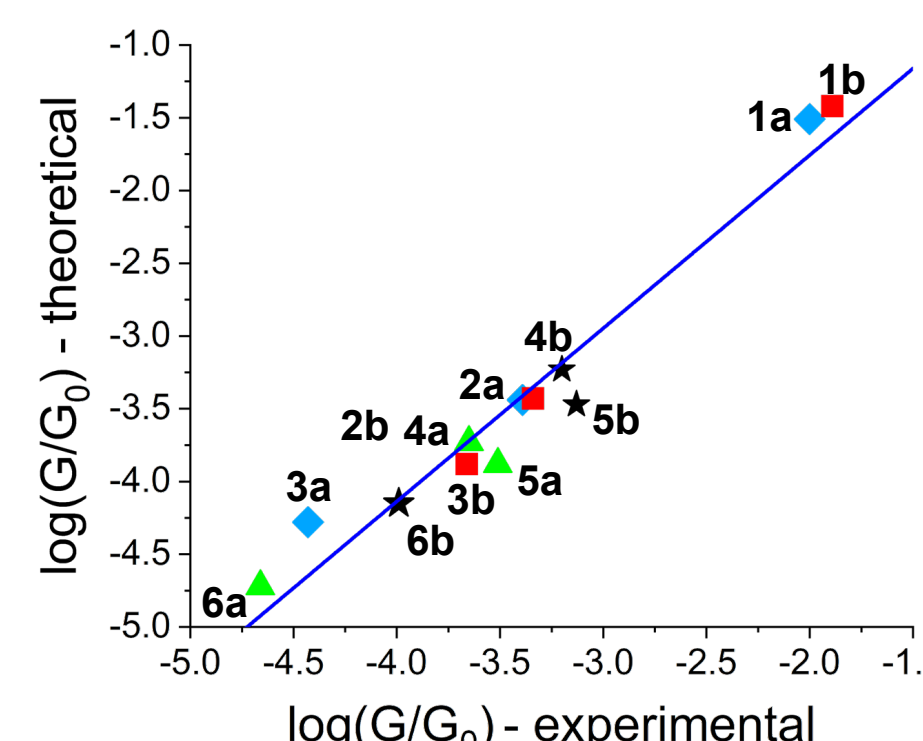
$\Delta E = \sqrt{E_{HOMO} - E_{Au}}$ , barrier height



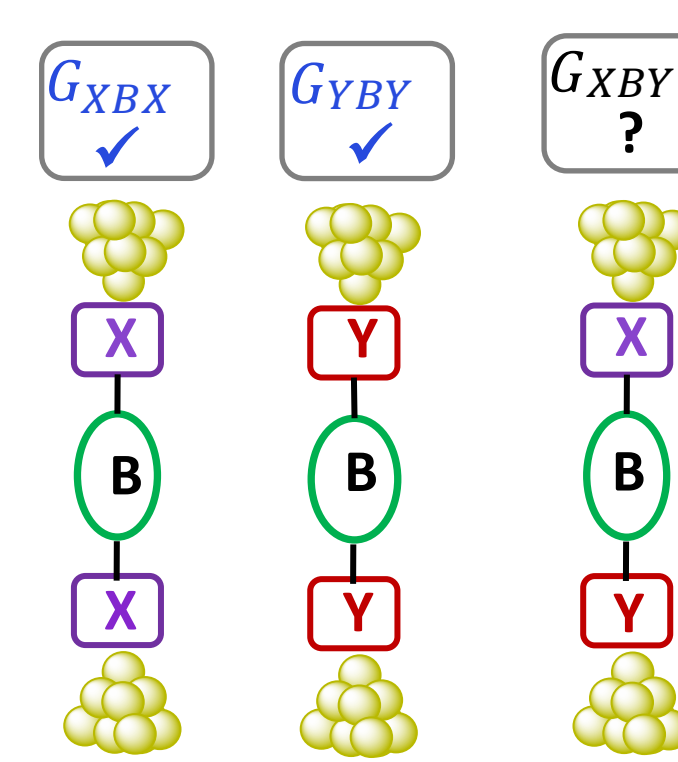
### Landauer-Büttiker model

$$G \approx \left(\frac{2e^2}{h}\right) T(E_F)$$

consider the alignment of Fermi energy with MO



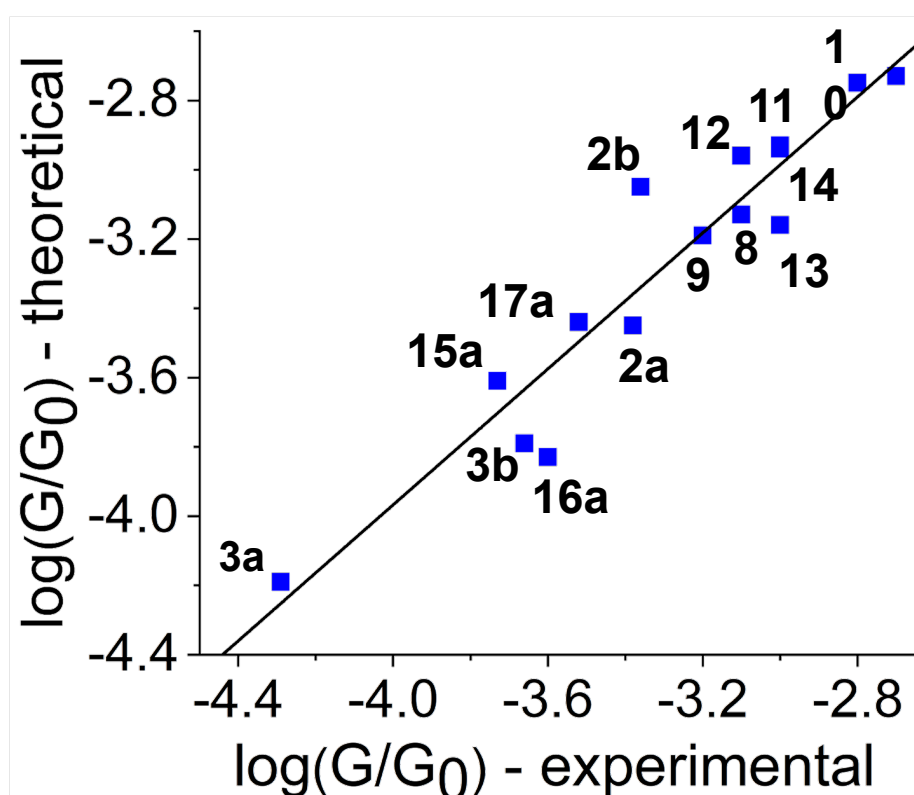
## Molecular Circuit Rules

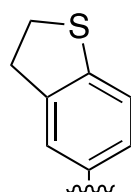
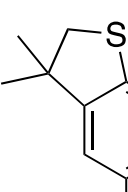
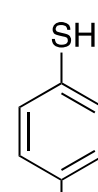
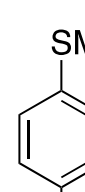
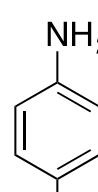


The molecular junction can be described in terms of **independent** ‘scattering’ regions allowing conductance to be partitioned into a sum of **contributions** from the ‘**anchor**’ and ‘**bridge**’ moieties, each described by a characteristic numerical parameter ( $a_x$ ,  $a_y$ ,  $b_B$ )

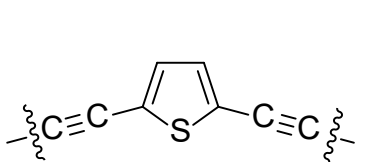
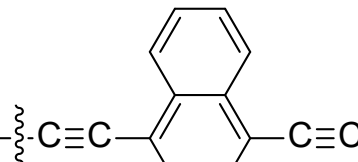
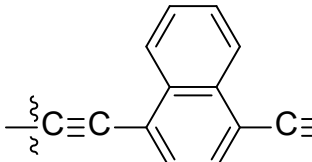
$$G_{XBY}^2 = G_{XBX} G_{YBY}$$

$$\log(G/G_0) = a_X + b_B + a_Y$$

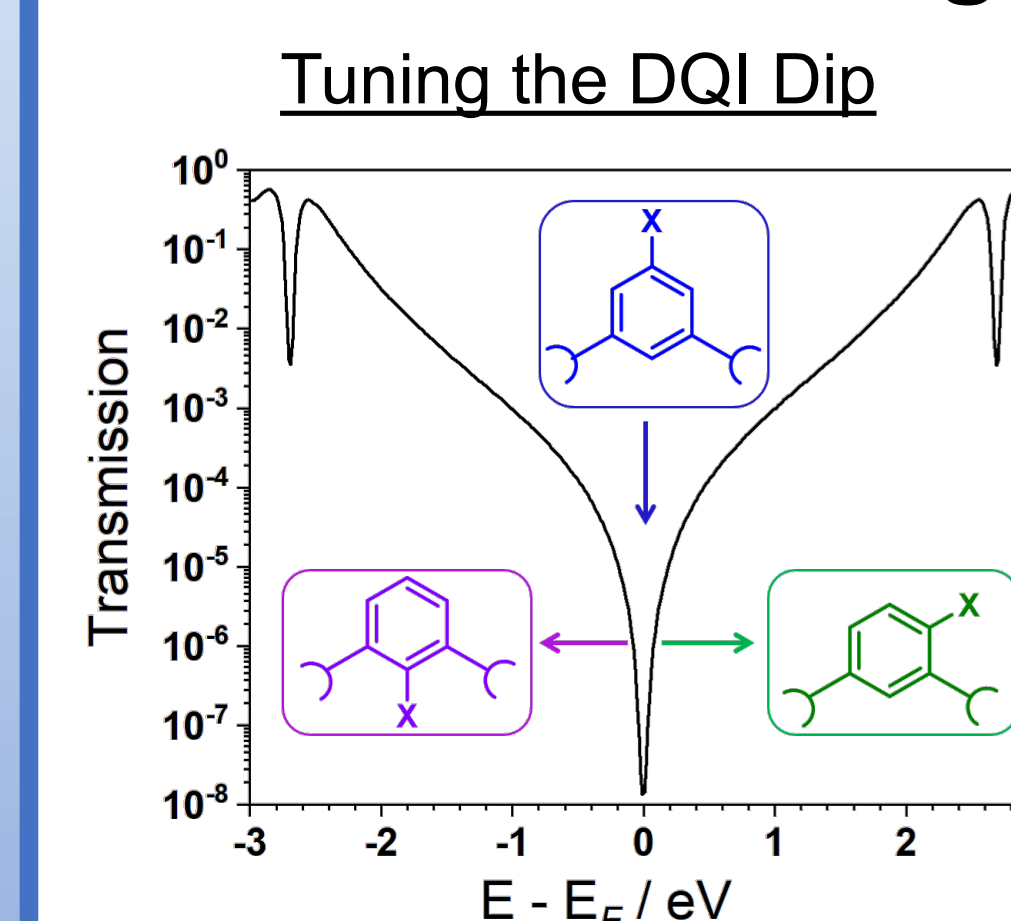
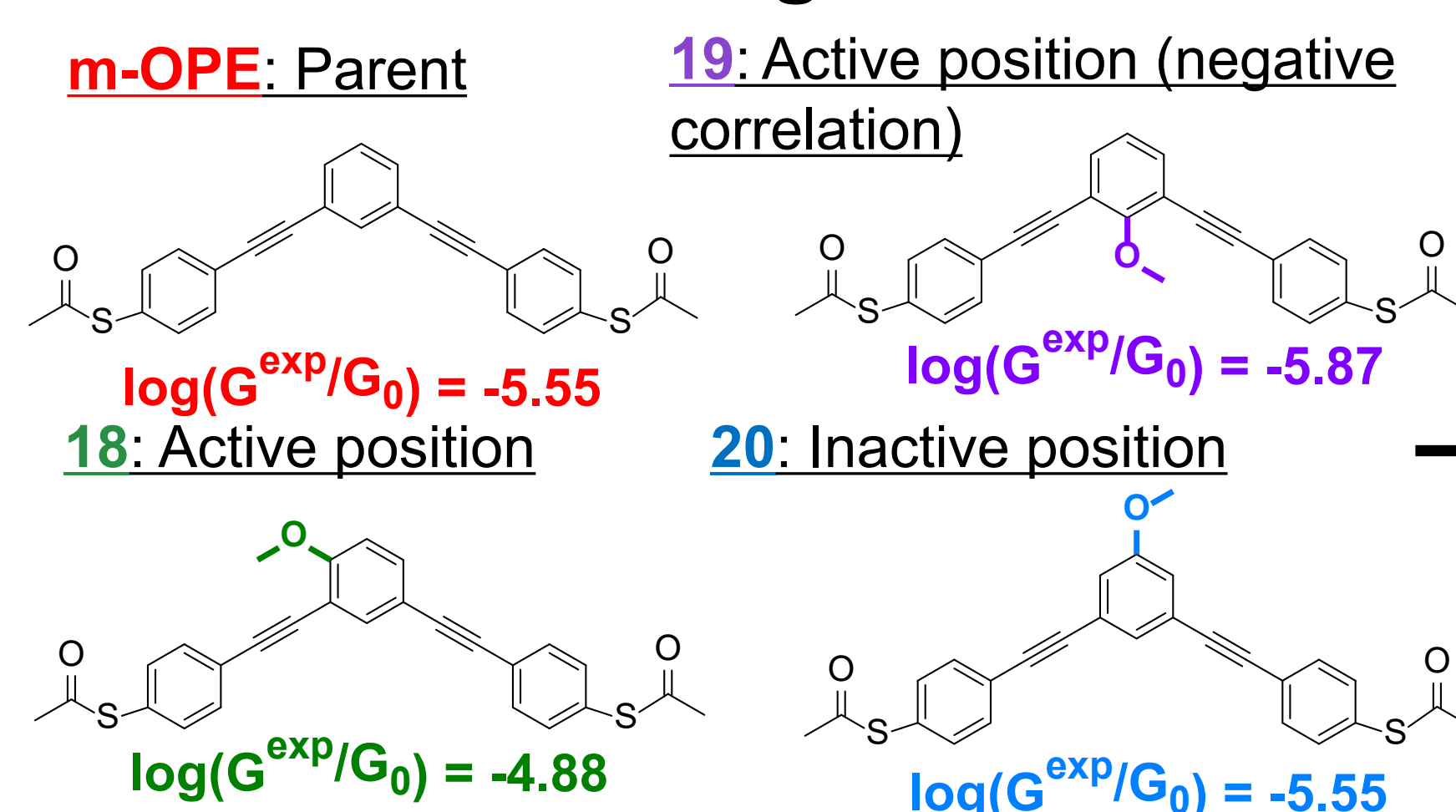


|                                                                                       |                                                                                       |                                                                                       |                                                                                       |                                                                                       |       |
|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------|
|  |  |  |  |  |       |
| BT                                                                                    | DMBT                                                                                  | SH                                                                                    | SMe                                                                                   | NH <sub>2</sub>                                                                       |       |
| $a_X, a_Y$                                                                            | -1.12                                                                                 | -1.21                                                                                 | -1.22                                                                                 | -1.41                                                                                 | -1.44 |

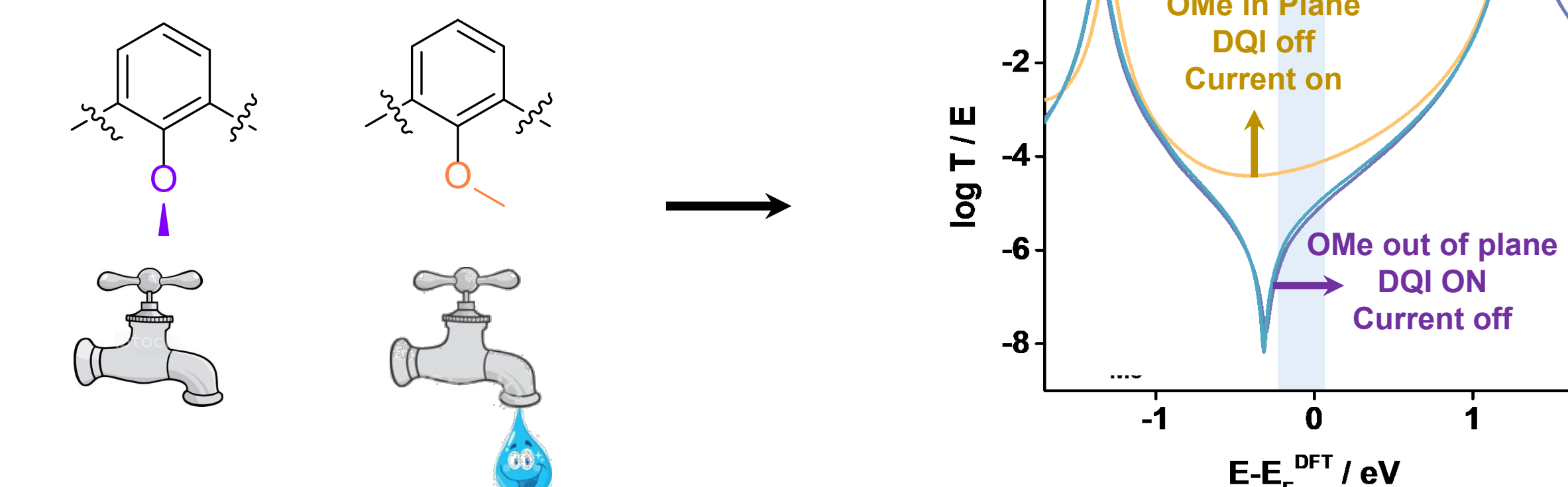
  

|                                                                                       |                                                                                       |                                                                                       |       |
|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------|
|  |  |  |       |
| $b_B$                                                                                 | -0.31                                                                                 | -0.63                                                                                 | -1.37 |
|  |  |  |       |
| $b_B$                                                                                 | -1.17                                                                                 | -1.39                                                                                 | -1.00 |

## Tuning Conductance Through Quantum Interference



The position of the DQI dip is proposed to be sensitive to the **position of substituents** on the bridge. Here we prove this relationships and show **conformation** of the pendant group is also a factor.



Two conformations of the “molecular tap” 19 changes the conductance from on to off.

## Conclusion

A series of both **organic** and **organometallic** compounds were studied in the junction to test the different concepts of the theory. We have found that the charge transport mechanism for single-channel transmission can be explained by both the **Landauer-Büttiker model** and the **Molecular Circuit rule**. Furthermore, the multiple channel transmission arises the **quantum interference** effect, which can be tuned by both position and conformation of the substituent.

## References

- C. J. Lambert, *Chem. Soc. Rev.*, **2015**, 44, 875-888.
- D. Z. Manrique, Q. Al-Galliby, W. J. Hong, C. J. Lambert, *Nano Lett.*, **2016**, 16, 1308-1316.
- M. H. Garner, G. C. Solomon, M. Strange, *J. of Phys. Chem. C*, **2016**, 120, 17, 9097-9103.
- M. Naher, S. Bock, Z. M. Langtry, K. M. O'Malley, A. N. Sobolev, B. W. Skelton, M. Korb and P. J. Low, *Organometallics*, **2020**, 39, 4667-4687.
- M. Naher, D. C. Milan, O. A. Al-Owaedi, I. J. Planje, S. Bock, J. Hurtado-Gallego, P. Bastante, Z. M. Abd Dawood, L. Rincón-García, G. Rubio-Bollinger, S. J. Higgins, N. Agrait, C. J. Lambert, R. J. Nichols and P. J. Low, *J. Am. Chem. Soc.* **2021**, 143, 3817-3829
- F. Jiang, D. I. Trupp, N. Algethami, H. Zheng, W. He, A. Alqorashi, C. Zhu, C. Tang, R. Li, J. Liu, H. Sadeghi, J. Shi, R. Davidson, M. Korb, A. N. Sobolev, M. Naher, S. Sangtarash, P. J. Low, W. Hong and C. J. Lambert, *Angew. Chem. Int. Ed.* **2019**, 58, 18987-18993.