

# Resolving band structure evolution and defect-induced states of single conjugated oligomers by scanning tunneling microscopy and tight-binding calculations

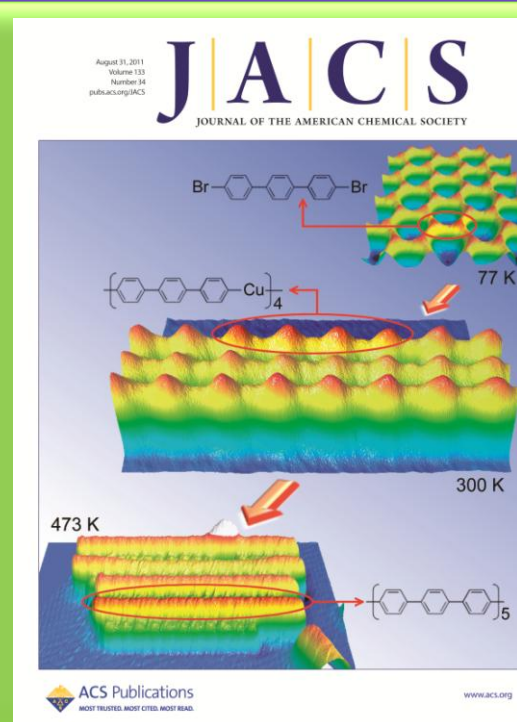
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Physical Review Letters 106, 206803 (2011)

Journal of The American Chemical Society 133, 13624 (2011)

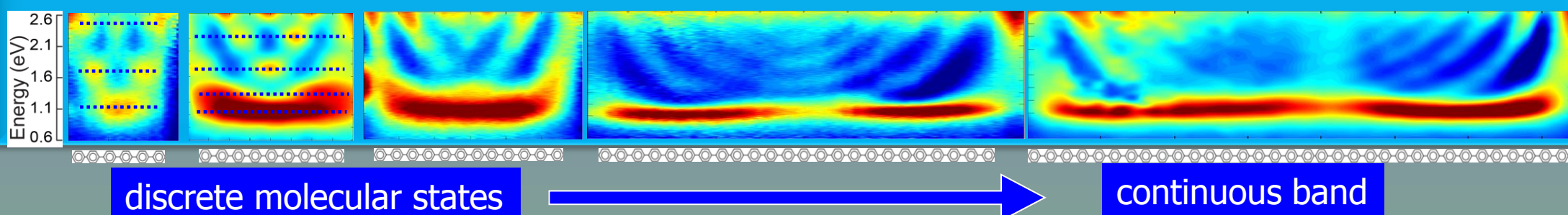
By means of cryogenic scanning tunneling microscopy and spectroscopy, we reveal a progressive development of a continuous conduction band out of discrete molecular orbitals as the length of the molecular oligomers increases. The experimental results are satisfactorily described by tight-binding calculations which gave a conduction band bandwidth of  $4.5 \pm 0.2$  eV and a band gap of  $3.1 \pm 0.2$  eV for an infinitely long polymer. In addition, we observe two types of defects, known as conformational torsional angle misfit and metasite kink. Tight-binding as well as density-functional theory model calculations confirm that both types of defects effectively destroy the delocalization.

**Sample Preparation:**  
Surface-supported  
Ullmann coupling



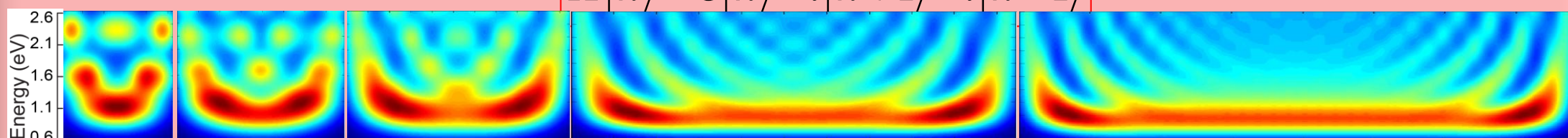
## Experimental Results: spatial distribution of density of states intensity

2 nm

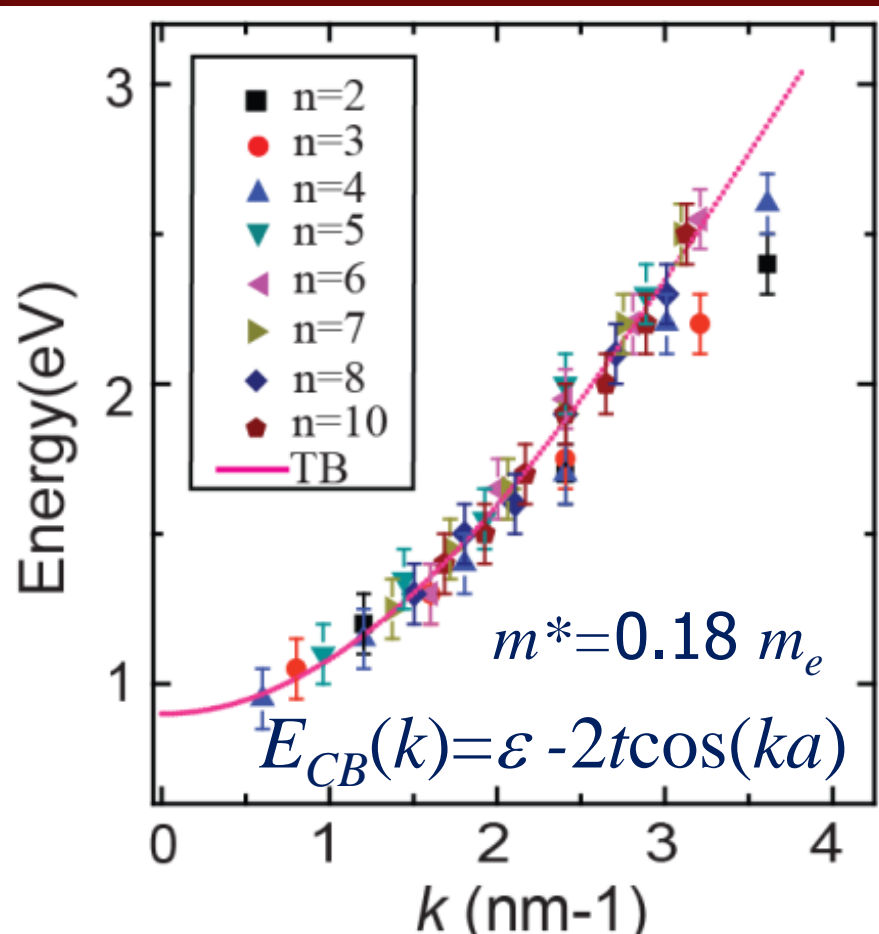


## Tight-binding Calculations:

$$H|n\rangle = \varepsilon|n\rangle - t|n+1\rangle - t|n-1\rangle \quad \varepsilon = 2.9 \text{ eV}, t = 1.0 \text{ eV}$$



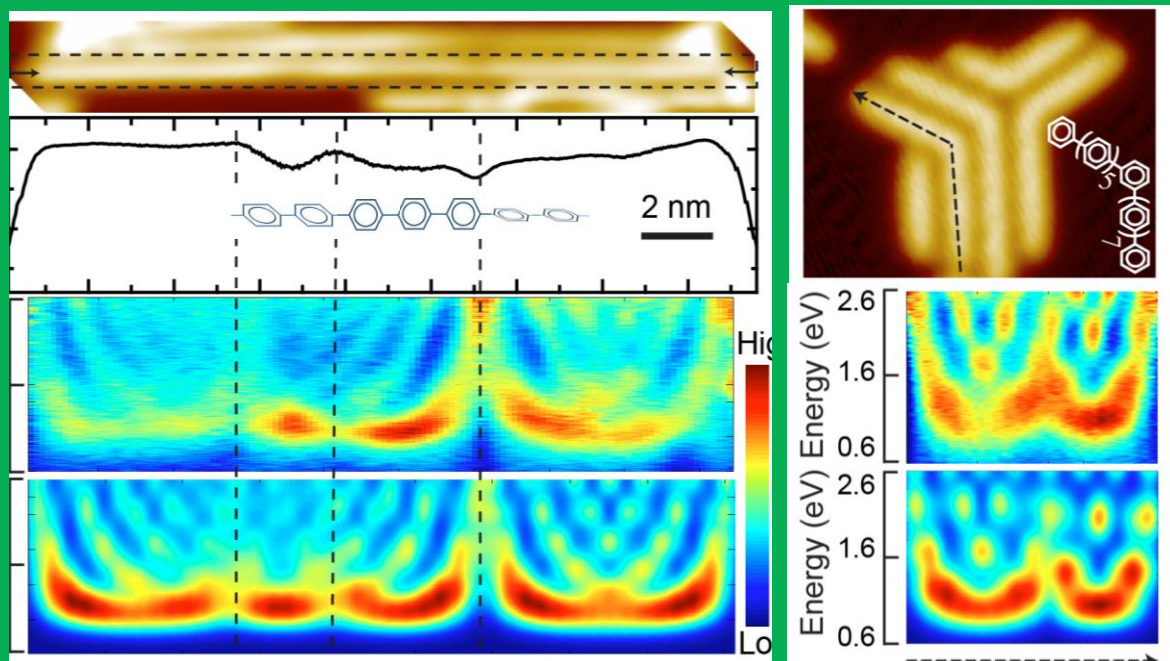
## Band structure



## Defect states

Torsional angle misfit

120° kink



**Both types of defects destroy the delocalization of the molecular states.**