Nanoelectronics
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Theoretical Modeling of DNA-based Biomolecular Nanowires

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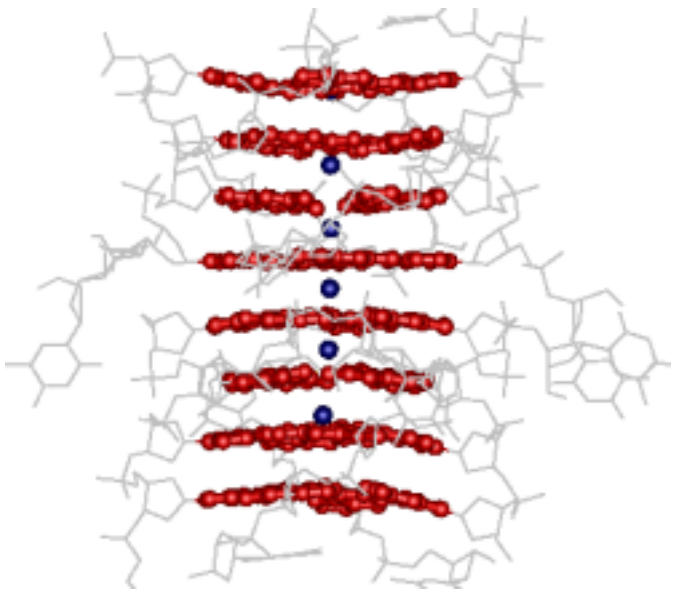

Collaborators

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Acknowledgements

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Computer time: CINECA Bologna, CICAIA Modena

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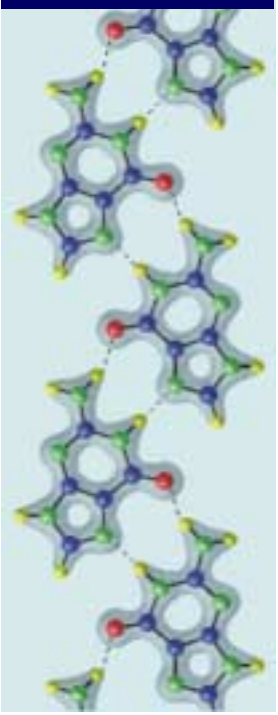
H-bonded G ribbon



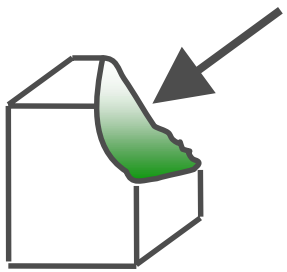
Outline

- Towards hybrid and mono-molecular electronics
  - Is DNA a viable electrical *material*?
- Experiments on DNA charge mobility
  - In the **Solid State**
    - Structure, conductivity
  - In **Solution Chemistry**
    - Guanine: low ionization potential ⇒ hole traps
- Guanine-rich stacks
  - Experimental results available, theoretical simulations feasible
  - π stacks, H-bonded ribbons, stacked & H-bonded G4
- DFT simulations: band transport contribution?
  - Energetics, electronic properties
  - G4: Flat bands, Effective semiconducting DOS
- Conclusions & Perspectives

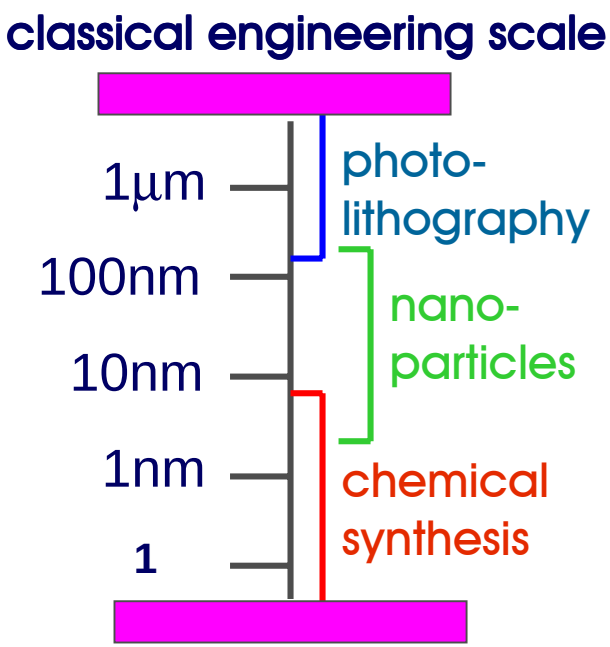
Electronics and Nano-Electronics

TOP-DOWN

"Sculpt" from bulk

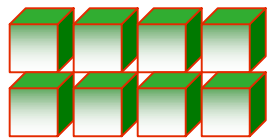


- Classical semiconductors



BOTTOM-UP

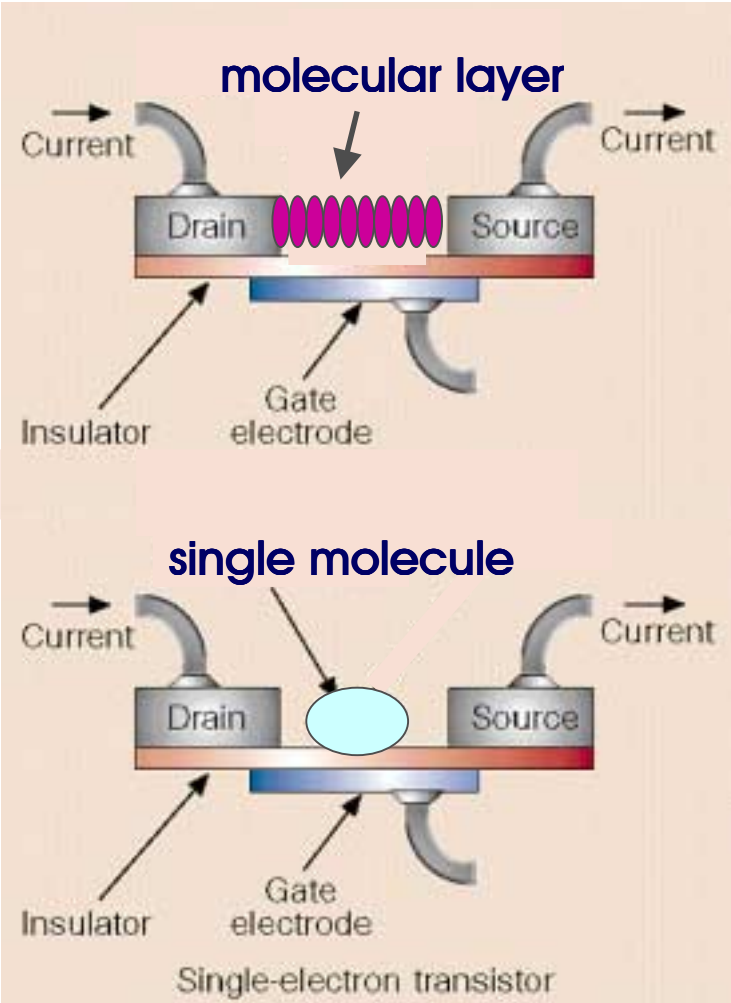
Assemble from nano-scale building blocks



- Molecular electronics
- Biomolecular electronics

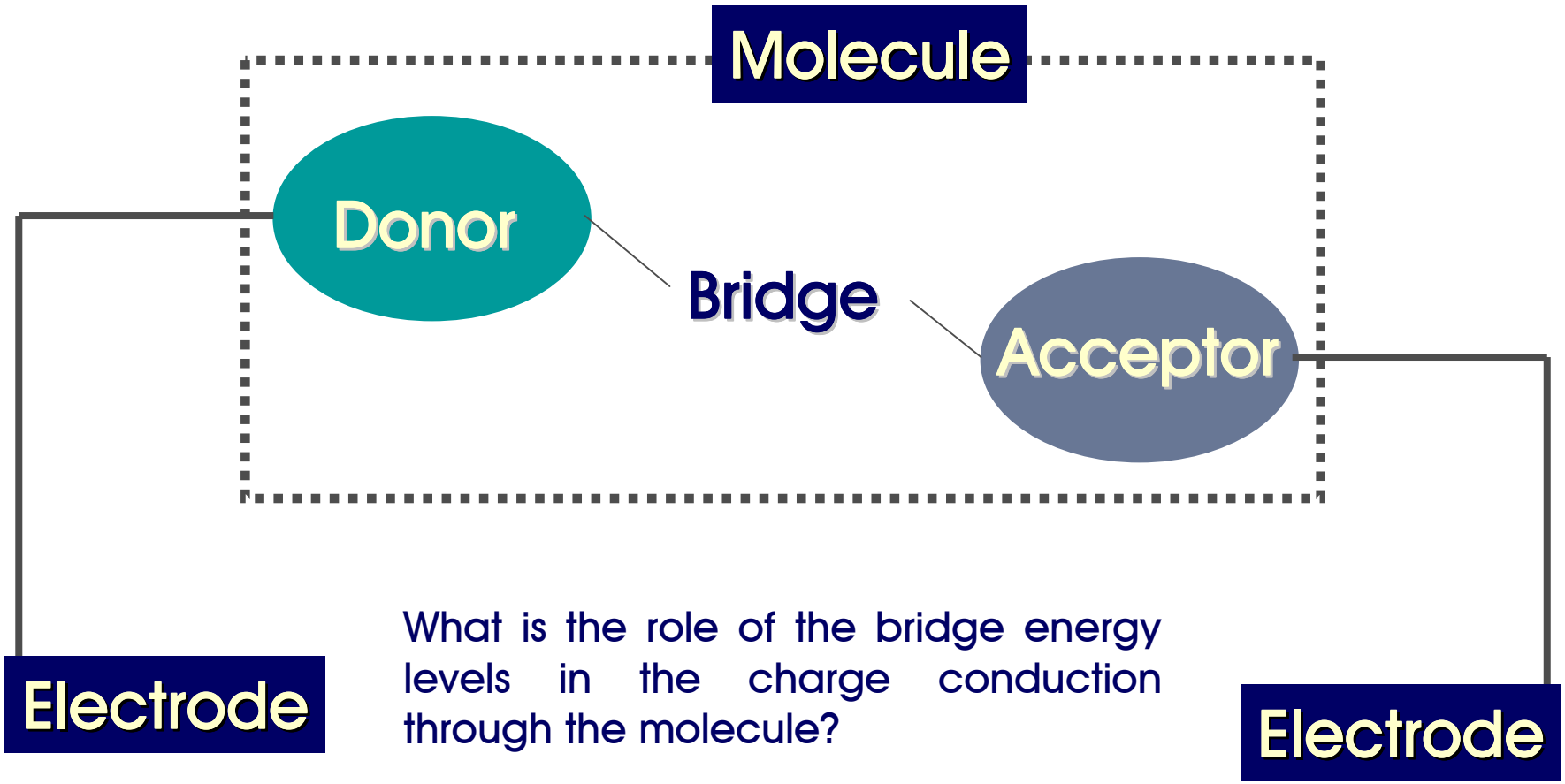
Biomolecular Electronics

the exploitation of functional properties of biomolecules (DNA, PROTEINS) to be used in hybrid electronic devices



- Peculiarities of Biomolecular Devices
  - Intrinsic Functionality
  - Self-Assembly
  - Intrinsically identical building blocks
  - Natural Nano-meter scale
- Self-assembled few-molecule monolayer
  - Tens-of-nanometers channel
- Single-molecule Bio-transistor
  - Few-nanometers channel
- Two-terminal devices are presently the prototype study-case

Molecular device scheme

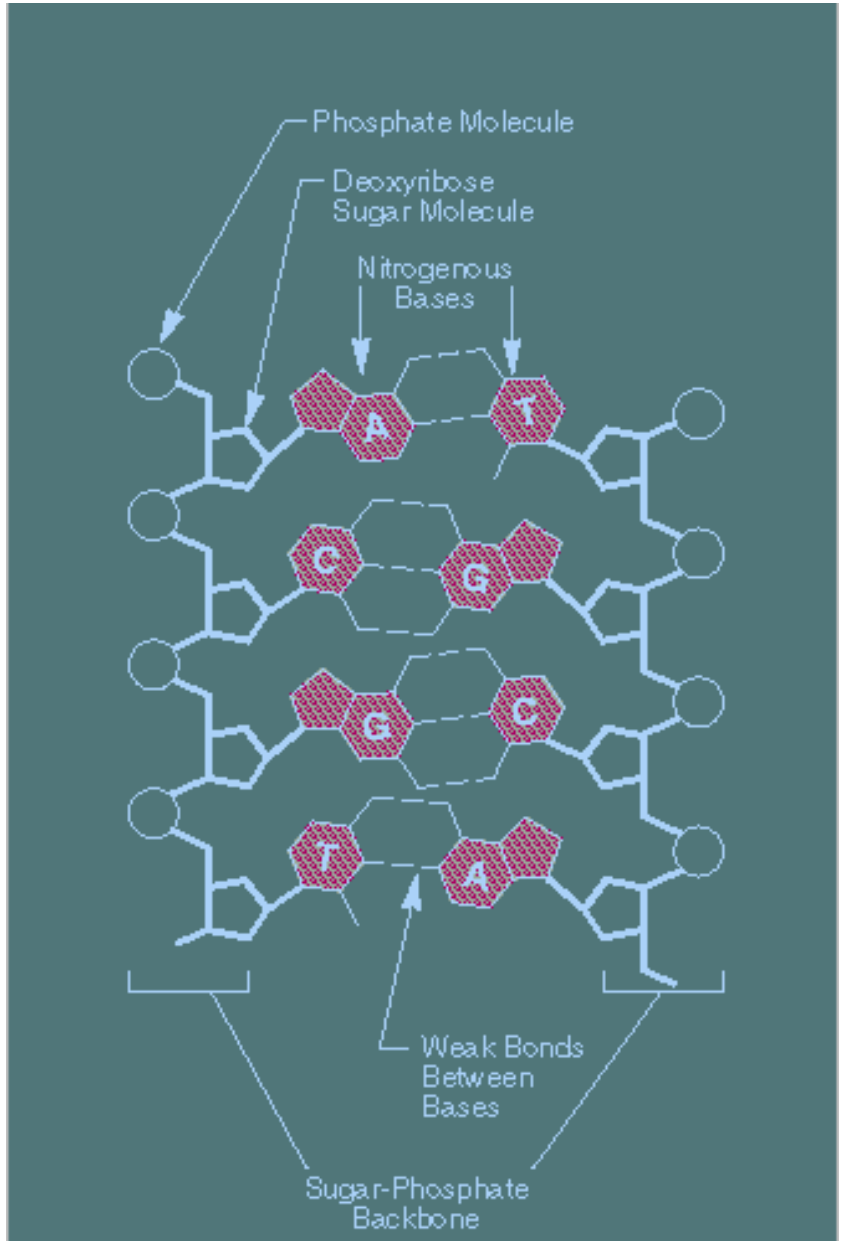


What is the role of the bridge energy levels in the charge conduction through the molecule?

Coupling: electrode-donor, donor-bridge-aceptor, acceptor-electrode

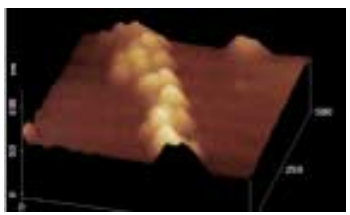
DNA Structural Features

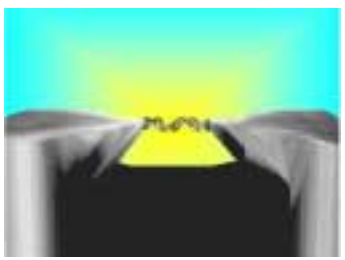
- Unique H-bonding base-base coupling
  - Guanine-Cytosine
  - Adenine-Thymine
  - Auto-recognition, Self-assembly
- Inner Core
  - Base-pair stack
  - Responsible for electron-hole mobility
- Outer backbone
  - Sugar-phosphate bridge connecting adjacent planes
  - May host mobile ions
- Protein recognition
  - Binding at specific sites of the sequence
  - Molecular nano-lithography



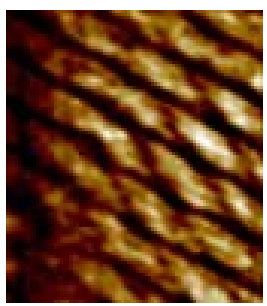
Selected experiments on DNA charge mobility

- Charge migration in DNA in Solution Chemistry
  - Donor-to-acceptor long-range electron transfer
  - Superexchange, hopping, polaron hopping (phonon-assisted)
  - J.K. Barton: distance independence, wirelike
- Electronic transport in DNA in device configuration
  - DNA as a template





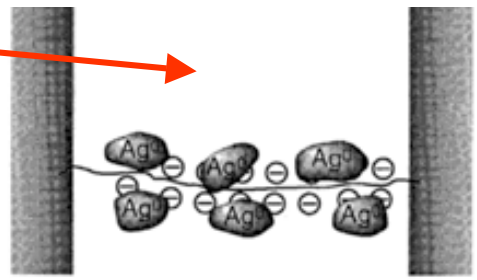
  - DNA as a (semi)conductor
  - Formation of extended states?



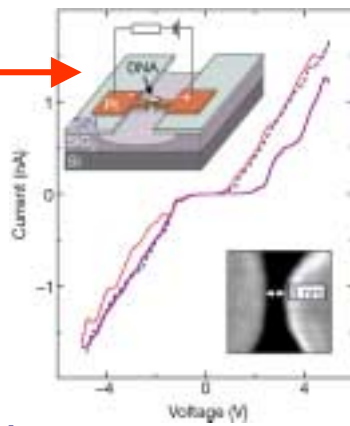
- Conductivity through deoxy-guanosine fibers

DNA in device configuration

- **Insulator**
  - 16-μm-long λ-DNA, 12-16-μm-spaced electrodes, single molecule
    - Braun et al., Nature 1998.
    - Template for conducting Ag wires.
  - 1.8-μm-long λ-DNA, SFM, single molecule
    - de Pablo et al., Phys. Rev. Lett. 2000.



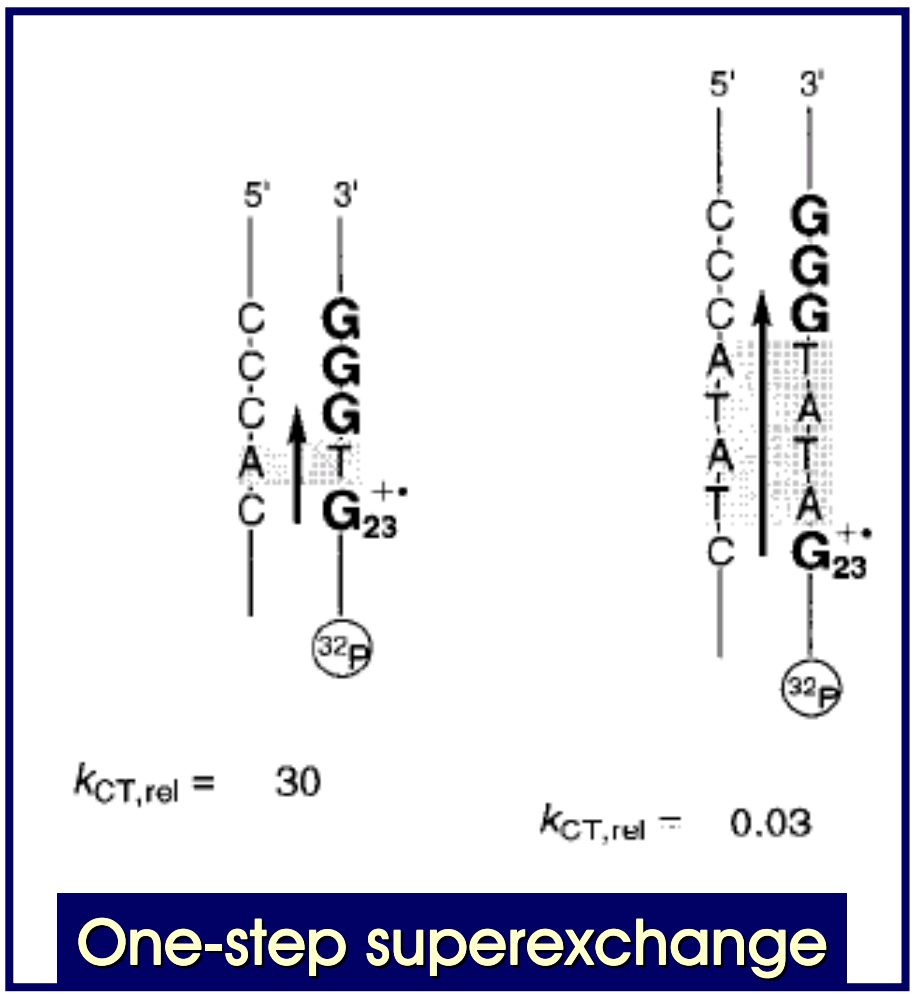
- **Semiconductor**
  - 10.4-nm-long (30 base pairs) poly(G)-poly(C), 8-nm-spaced electrodes, single molecule
    - Porath et al., Nature 2000.

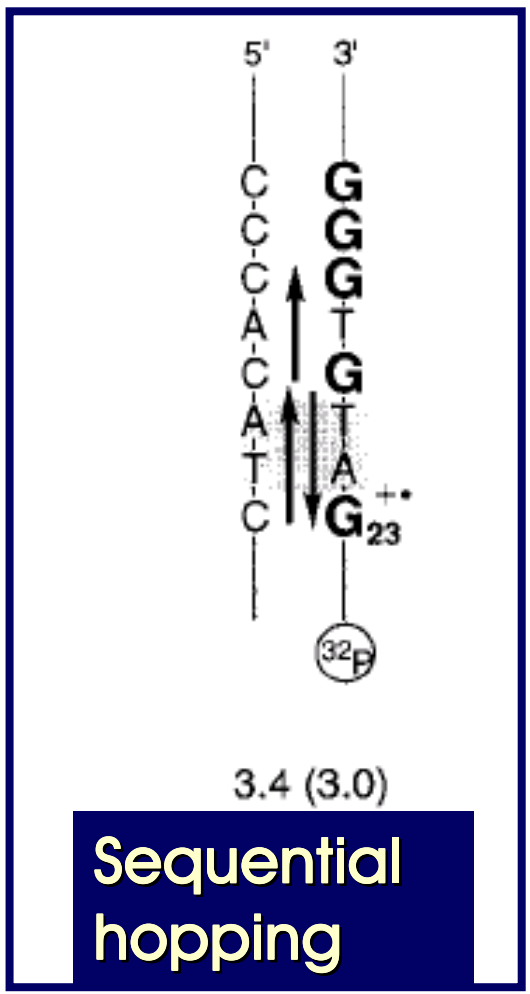


- **Conductor**
  - 600-nm-long λ-DNA, bundles in 2-μm holes
    - Fink & Schönenberger, Nature 1999.
- **Superconductor** (proximity-induced superconductivity)
  - 16-μm-long λ-DNA, 0.5-μm-spaced electrodes, few molecules
    - Kasumov et al., Science 2001.

E. Meggers et al., *J. Am. Chem. Soc.* **120**, 12950 (1998)

Experiment: hole transfer





Mechanisms for DNA charge motion

One-step tunneling, Marcus & Sutin, Biochim. Biophys. Acta (1985).

Rate $k = (1/h)\, V_0^2\, F \exp(-\beta R)$
[structureless wide 1D barrier]

Multi-step process, transfer of localized charge, slow distance dependence

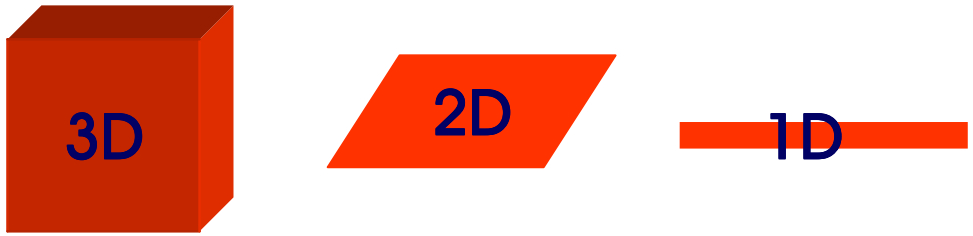
E. Meggers, *JACS* 1998. Jortner, *PNAS* 1998.

Hints

- From experiments in the *solid state*
  - Fix constraints on wire variability
    - Sequence
    - Length
    - Aggregation state
- From experiments in *solution chemistry*
  - Outstanding role of the Guanine base

Our approach

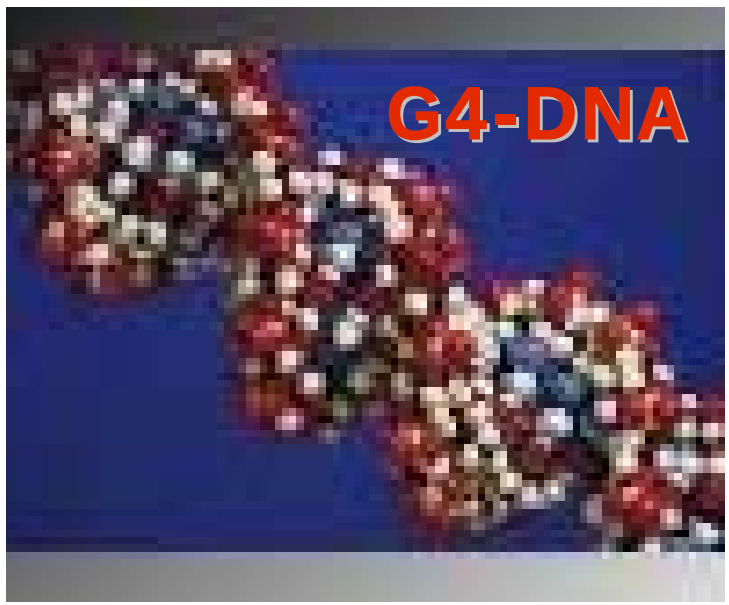
- **Inorganic nano-wires**
  - Starting point: 3D crystal
    - Delocalized orbitals
    - Bandstructure
  - Confinement in 2 directions
    - Energy quantization perpendicular to wire axis
    - Residual band dispersion along wire axis



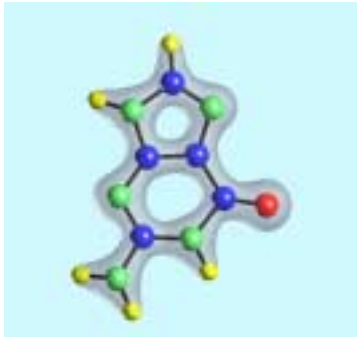
- **(Bio)Molecular nano-wires**
  - Starting point: molecular building blocks
    - Localized orbitals
    - Discrete energy levels
  - Periodicity in 1 direction $\rightarrow$ 1D crystal lattice and bandstructure
    - Orbital delocalization & band dispersion along wire axis?
    - Under which conditions?

Motivations for selecting G4 wires

- G-aggregates
  - Ribbons, tetrads, DNA sequences
  - Role of G and $(G)_n$ in DNA damage and electron transfer
- Tetrad stacks: well characterized real systems, X-ray and NMR data available
- Very stable in different chemical environments
  - With and without sugar-phosphate backbone
  - Stabilized by metal cations in the core
  - Mechanically resistant (up to ~1 μm)
- Different preparations viable
  - From single strands and double strands
  - Properties tuned by metal selectivity
- Only guanine ⇒ no sequence dependence
- Appealing to study transport properties of guanine-rich self-assembled supramolecular wires

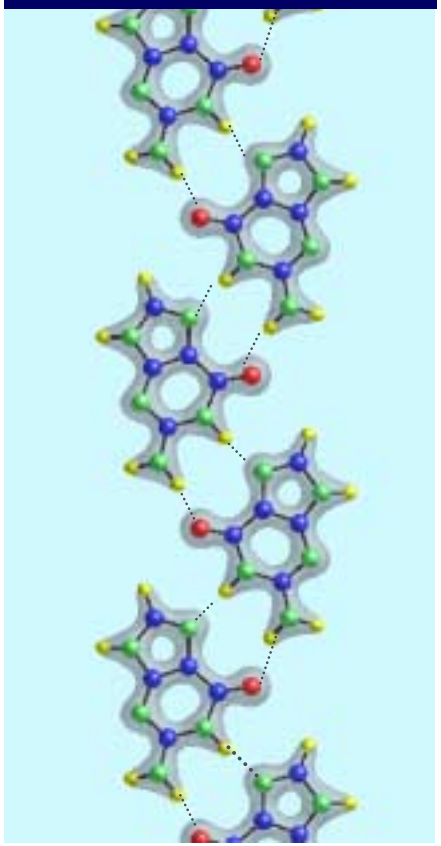


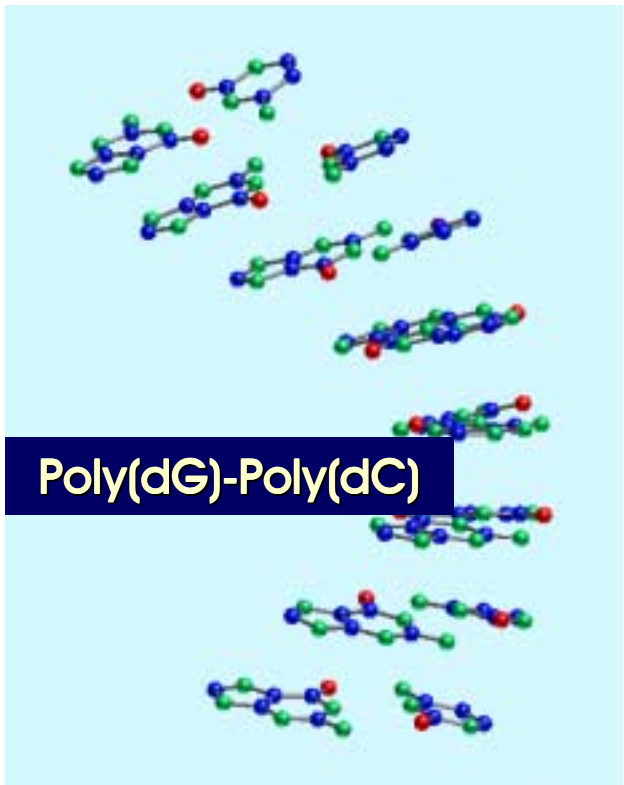
G-aggregates



Guanine

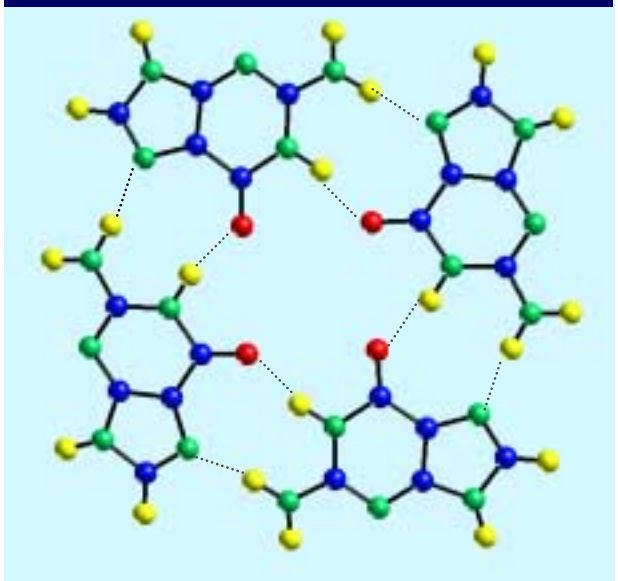
H-bonded ribbon





Poly(dG)-Poly(dC)

H-bonded quartet

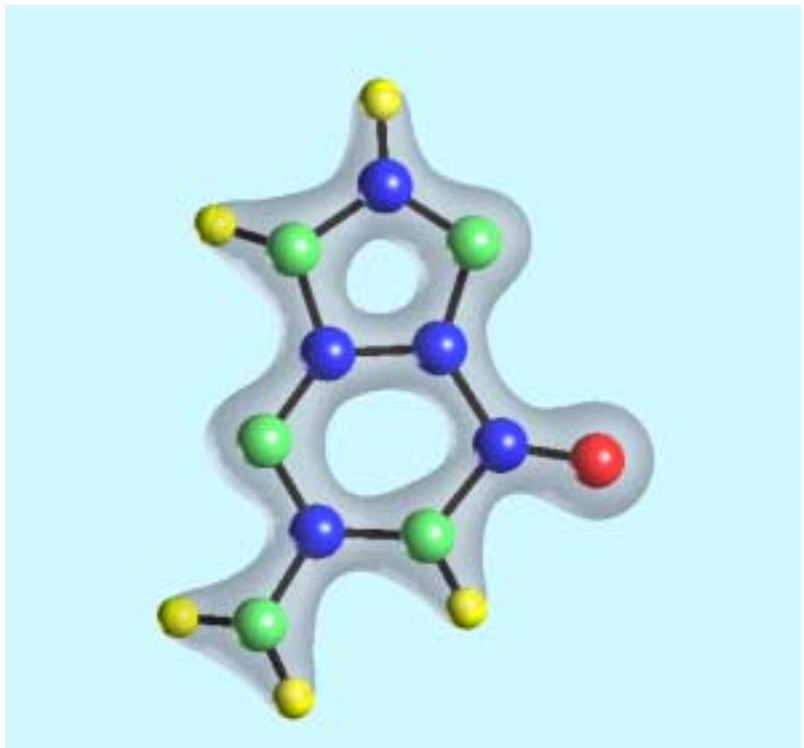


Method

- Structural Optimization
  - DFT-GGA (BLYP), ab-initio soft pseudopotentials (M&T), plane wave basis, periodically repeated supercells, BZ sampling along the wire axis
    - Atomic displacement until forces vanish (within 0.05 eV/Å)
    - Suitable to describe structures with long-range order $\rightarrow$ 1D wires
  - C,N,O: hard cores $\Rightarrow$ many plane waves needed, 50 Ry cutoff
  - Large supercells (6×10^3 Å^3), 195 atoms, thick vacuum
  - Tests on isolated G molecules and H-bonded G ribbons
- Relative formation energies
  - Dependence on the atomic and electronic (E_F) chemical potentials
- Electronic properties
  - Bandstructure
  - Density of States

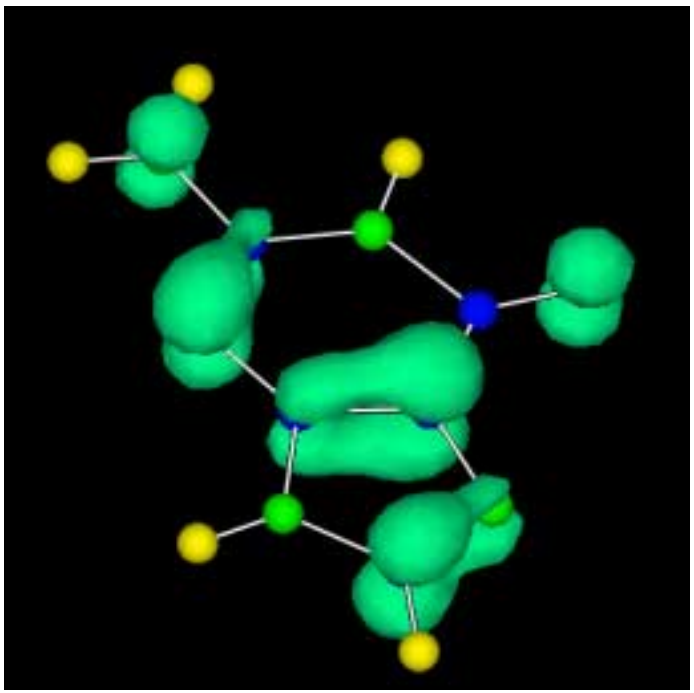
Building block: the Guanine base

- Carbon, Nitrogen, Hydrogen, Oxygen
- Bond lengths: 2%
- Bond angles: 1%
- HOMO and LUMO: π character

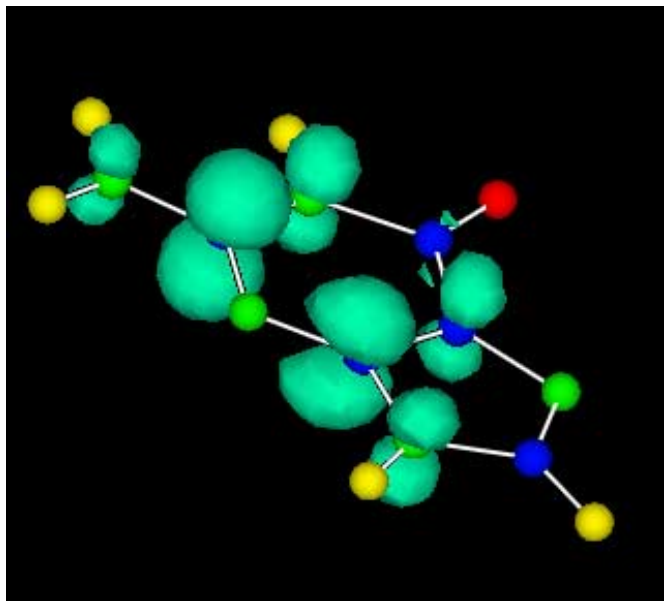


Isolated guanine molecule

Isolated G: electron states



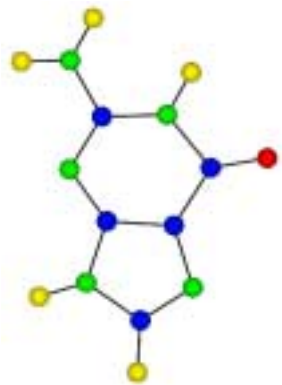
HOMO: π character
Localized on C-C and
C-N bonds

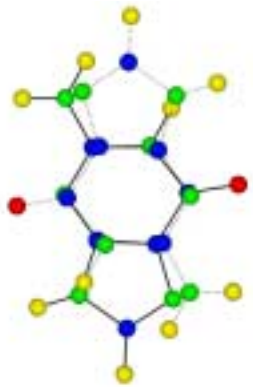


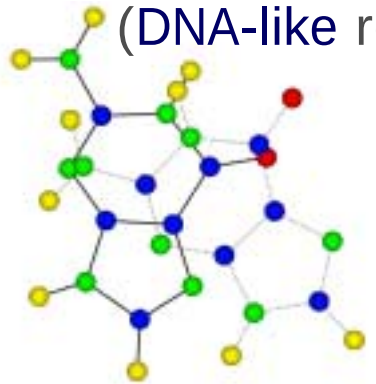
LUMO: π character
E_{LUMO}-E_{HOMO}=4.8 eV
Localized on atoms

Suitable for π-π interactions in G stacks

Guanine stacks



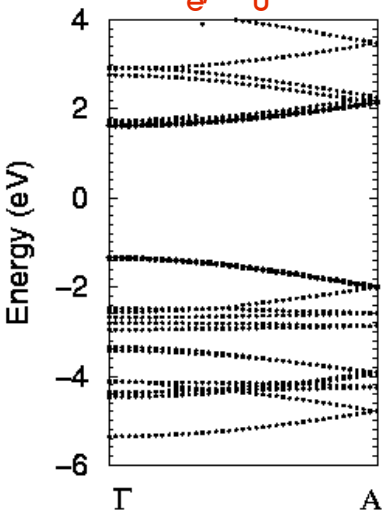




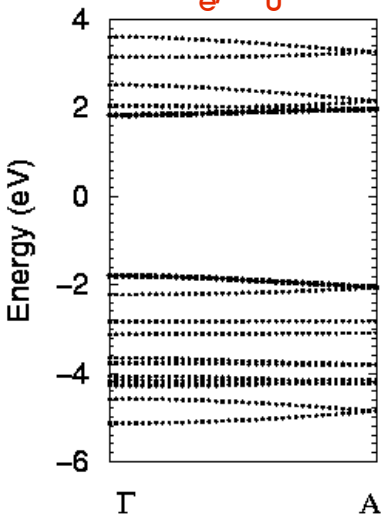
(DNA-like rot)

Bandstructure along the stacking direction

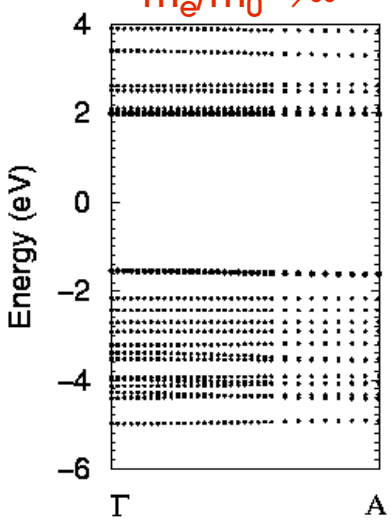
$m_e/m_0 \sim 1$



$m_e/m_0 \sim 2$

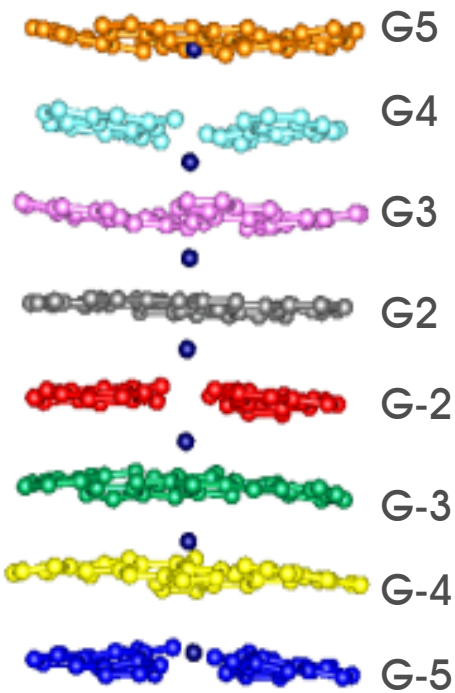


$m_e/m_0 \to \infty$



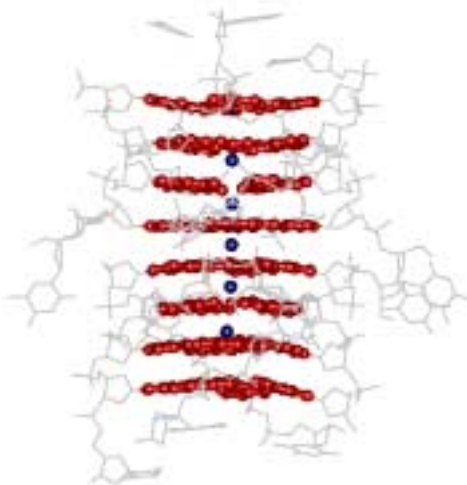
R. Di Felice et al., Phys. Rev. B **65**, 045104 (2002)

G4-wires: structure



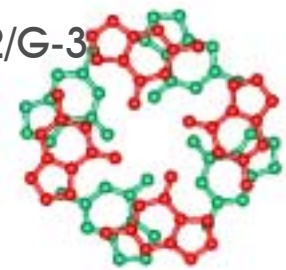
Side view

Top view

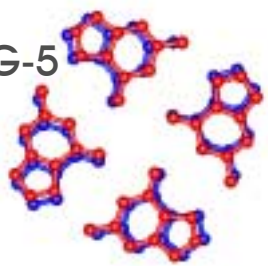


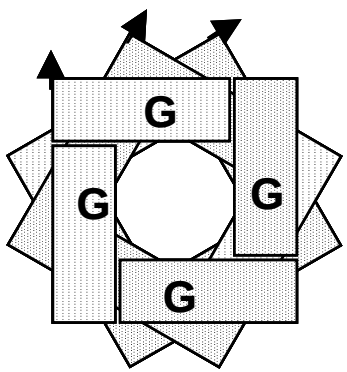
X-Ray Structure UDF062
K. Phillips et at., J. Mol. Biol. 1997

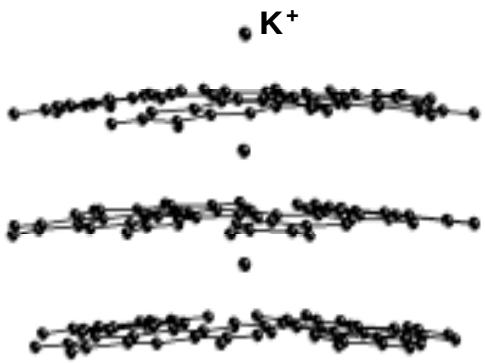
G-2/G-3



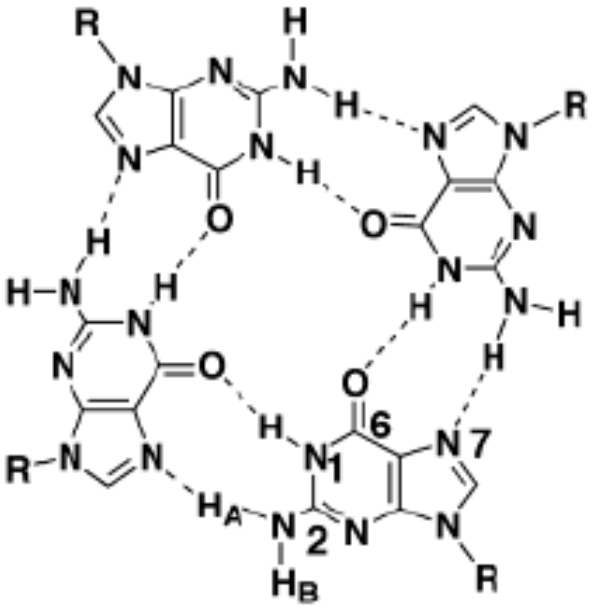
G-2/G-5



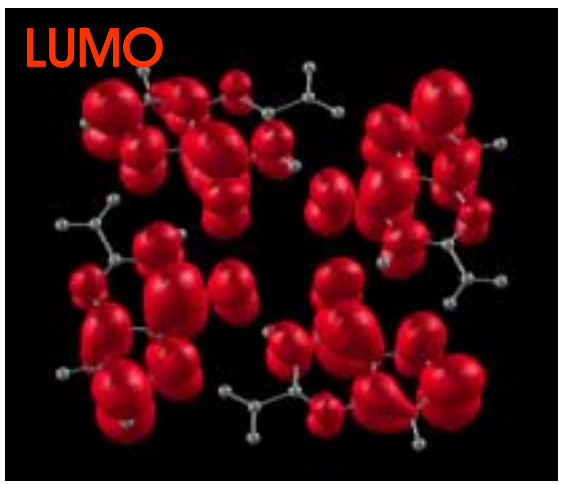




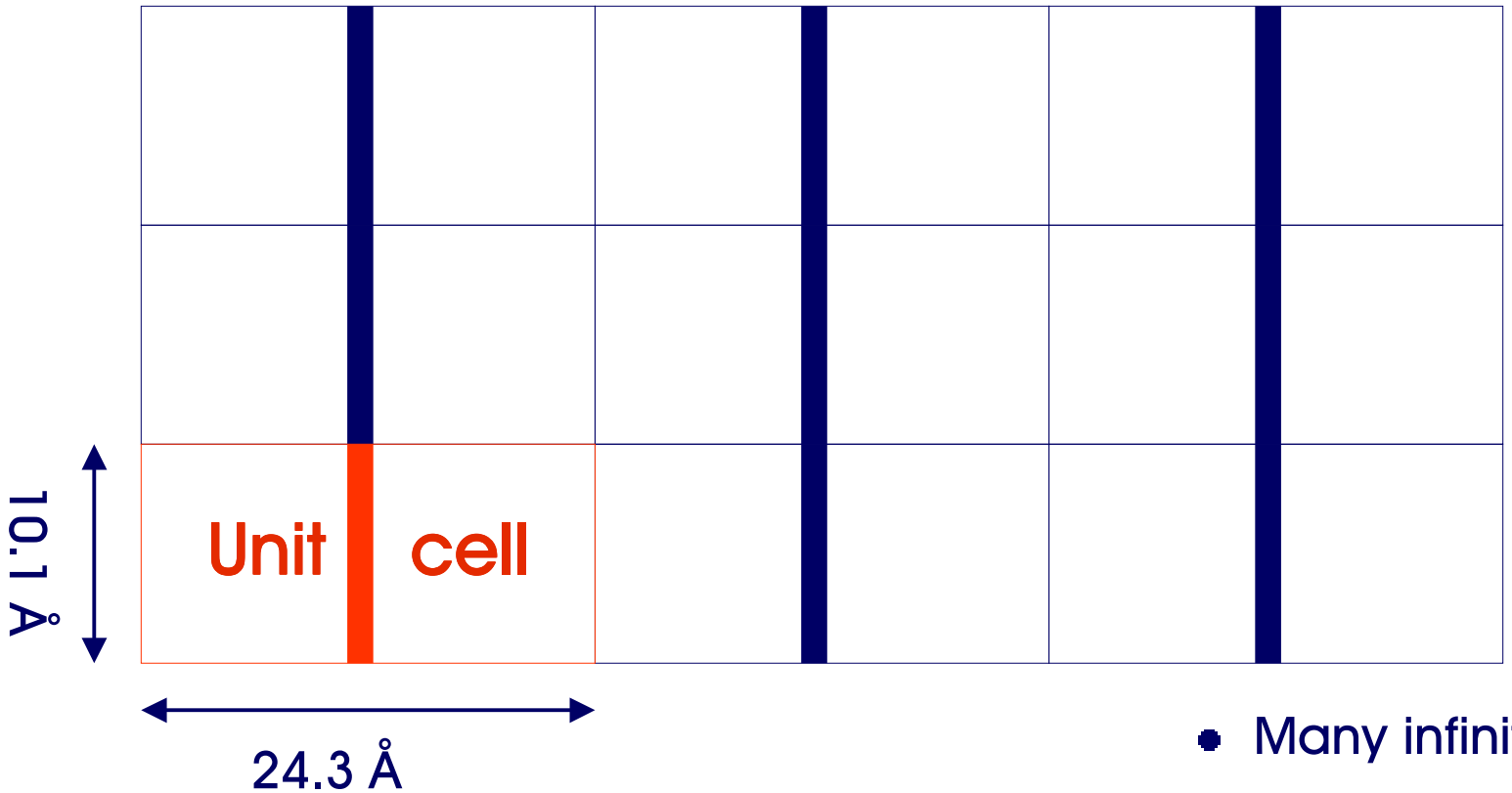
The planar tetrad



- Double ring of H-bonds
- Electronegative inner core, O atoms
- Thermodynamically stable
- No in-plane orbital delocalization



Periodic boundary conditions

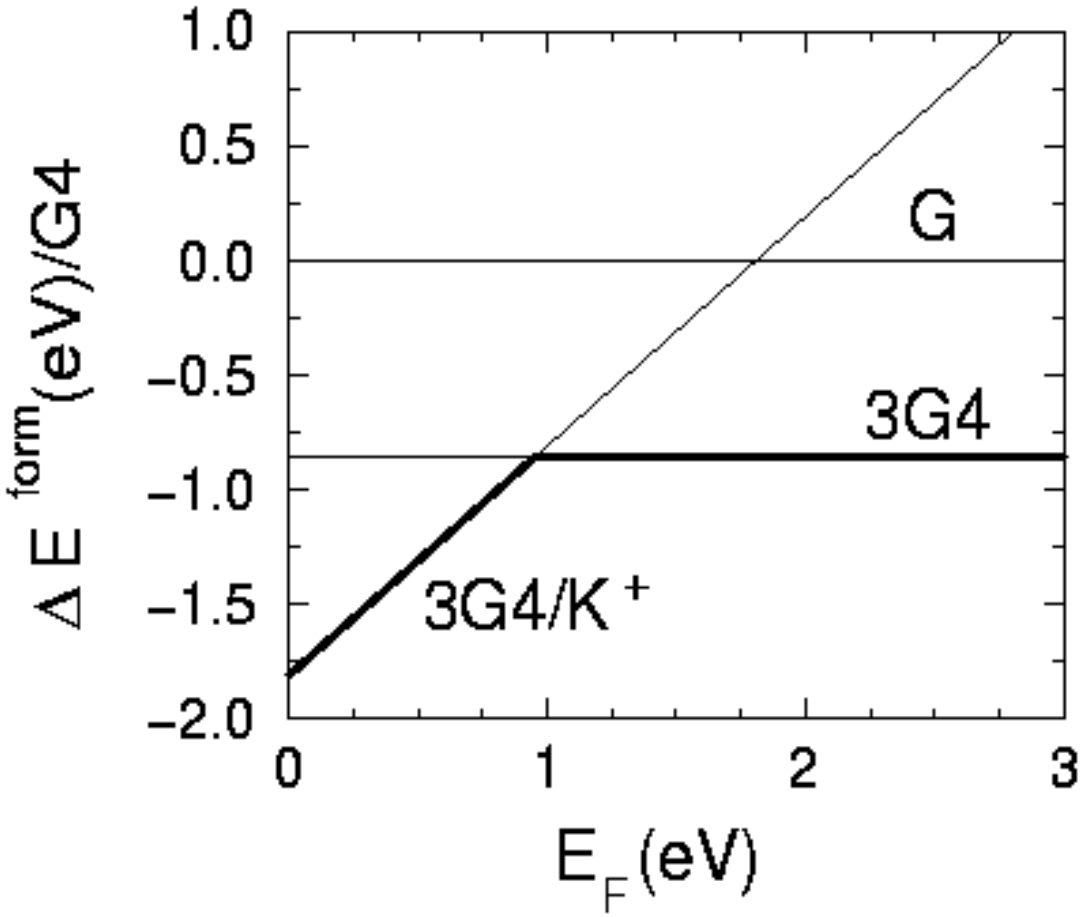


- Many infinite wires
- Wire thickness ~ 10 Å
- Avoid inter-wire spurious coupling → large distance

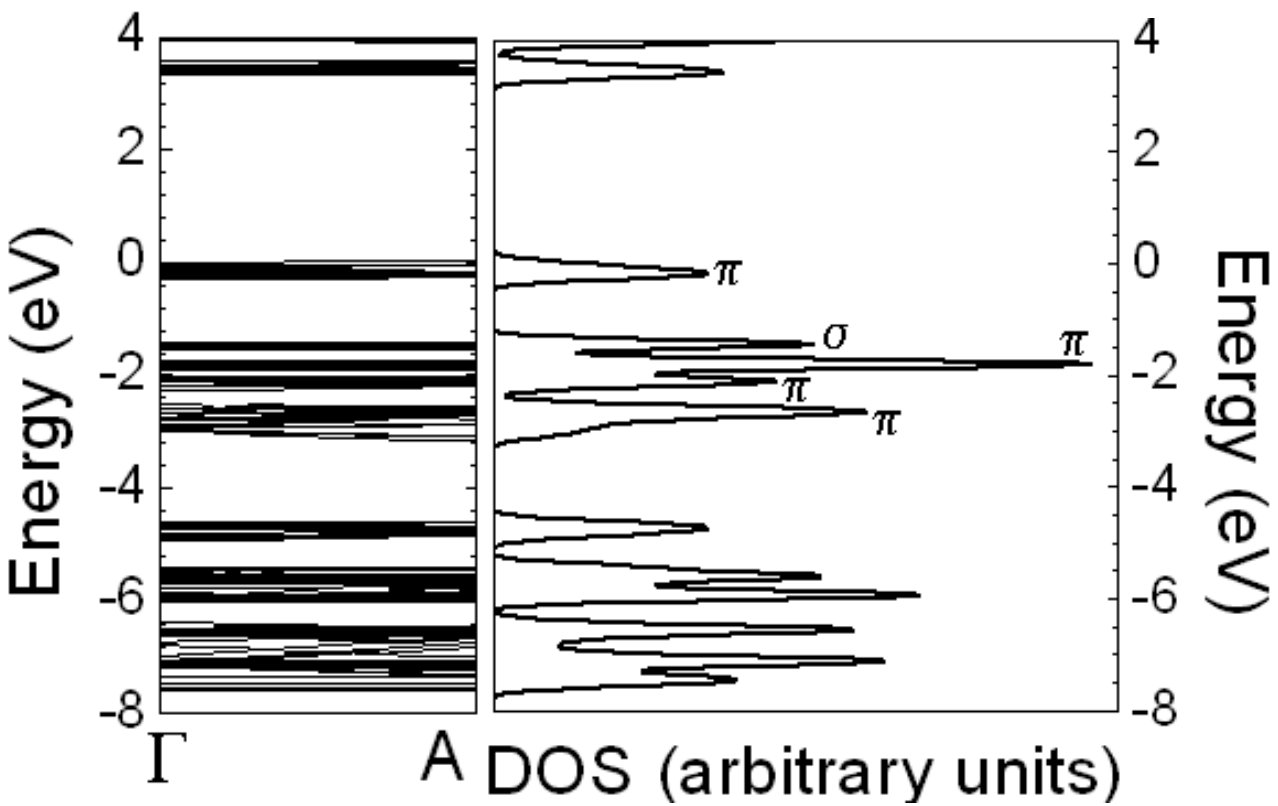
G4 Stability

- K-rich conditions
  - $\mu^K = \mu^{K(bulk)}$
  - $\Delta n^K = \Delta n^e = 3$ for $3G4/K^+$
- Variable Fermi level
  - Linear dependence
  - Stable wires
  - $3G4/K^+$ favored for $E_F <$ 1 eV
  - Fermi level pinning at the HOMO ($E_F = 0$) consistent with the presence of cations
- Metal cations stabilize the extended nanowires

$$\Delta E^{form} = \Delta E^{tot} - \Delta n^K \mu^K - \Delta n^e E_F$$

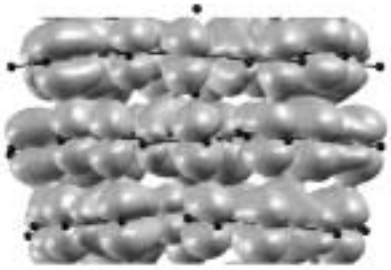


G4 Electronic Properties

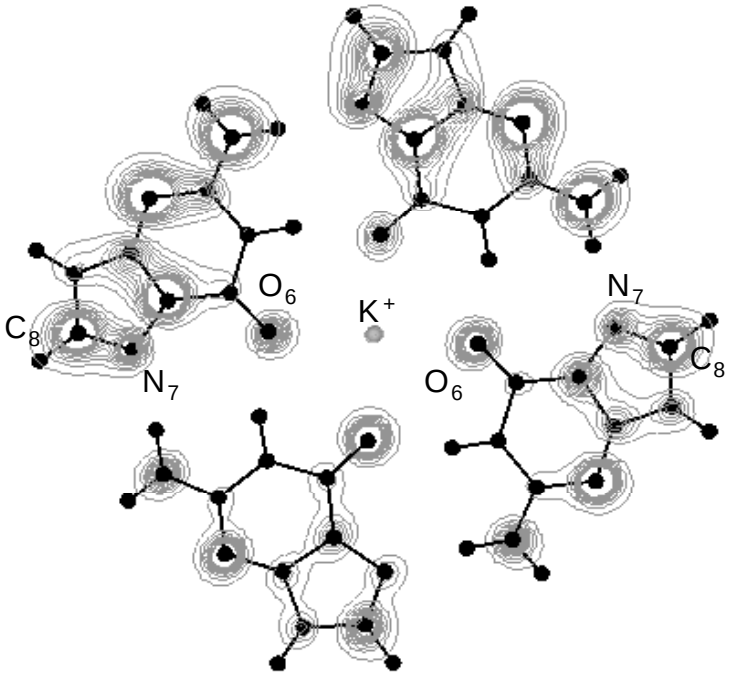


- **Bandstructure**
  - Flat bands
  - No dispersion along wire axis (Γ-A)
  - Minibands
- **DOS**
  - Peak spreading from minibands
  - π-like and σ-like
  - Effective semiconductor

A. Calzolari et al., Appl. Phys. Lett. **80**, 3331 (2002)

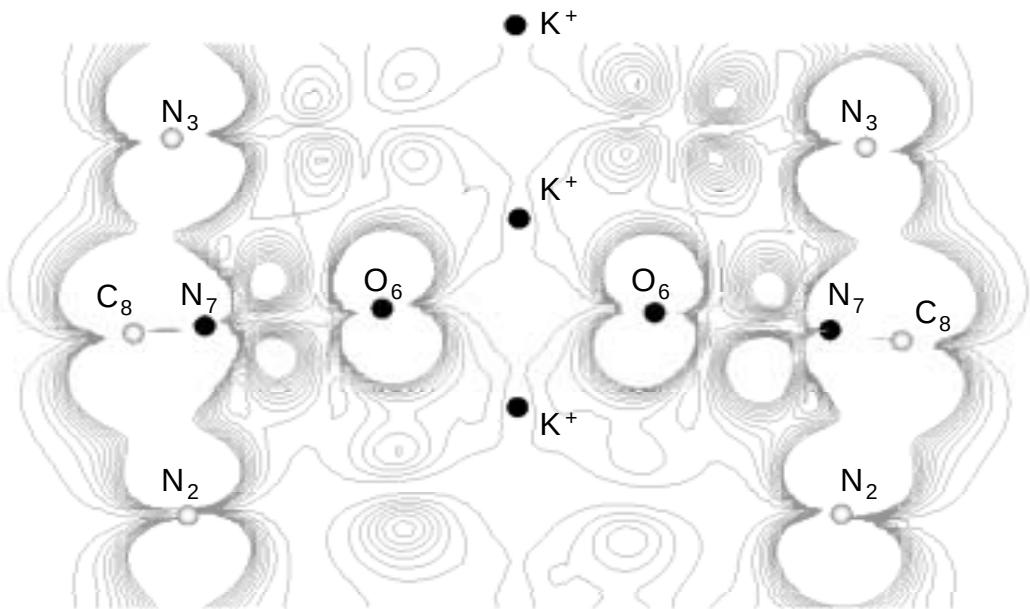


G4 Electron orbitals



Delocalization along wire axis

- Channels for charge motions
- Through the bases, not through the inner core



Linear combination of almost degenerate HOMO's (~20 meV)

Conclusions

- Stability of G4-based columnar stacks in the presence of K^+ ions
- π-π superposition insufficient to induce band dispersion along the wire axis
- Minibands from closely spaced energy levels
- Possible thermal coupling
  - Combination of orbitals leads to delocalization
- Effective behavior of wide-bandgap semiconductors
- Appealing candidates for biomolecular electronics

Perspectives

- **G4**: Effects of other metal cations
  - Stability
  - Electronic properties
    - Tuning by different metals: effective doping, transport mediation
    - Relation between disctrete charge transfer and *continuous* charge transport

- Other **nucleotide-based** structures that may function as good molecular **wires**

- Implementation of methods for ab-initio computation of the quantum conductance and transport characteristics