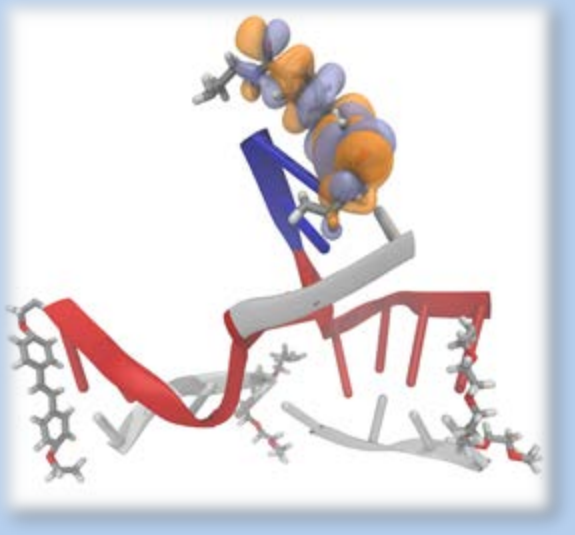
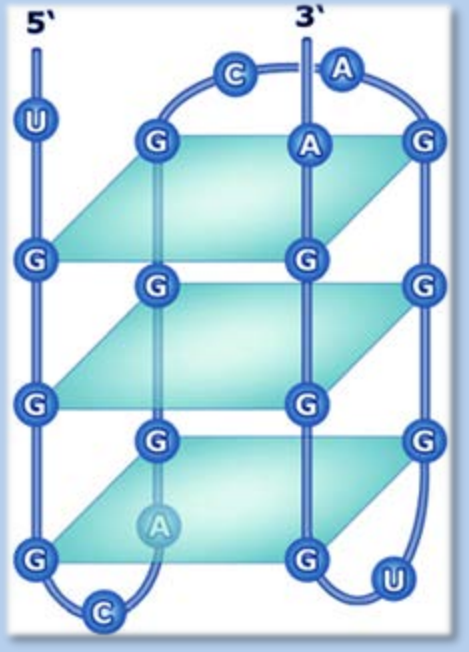




Council on Ionizing Radiation Measurements and Standards 2015
Gaithersburg, MD at NIST, April 27-29, 2015
Working Group Session "The use of Ionizing Radiation in Synthesis of Advanced Materials"

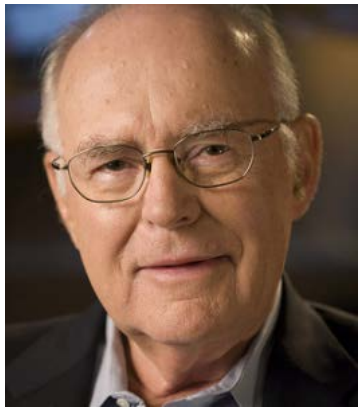
Recent Developments in Charge Transport in DNA-Based Electric Devices:

Charge Flow across Practically Important Molecular Constructs with Complex Architecture

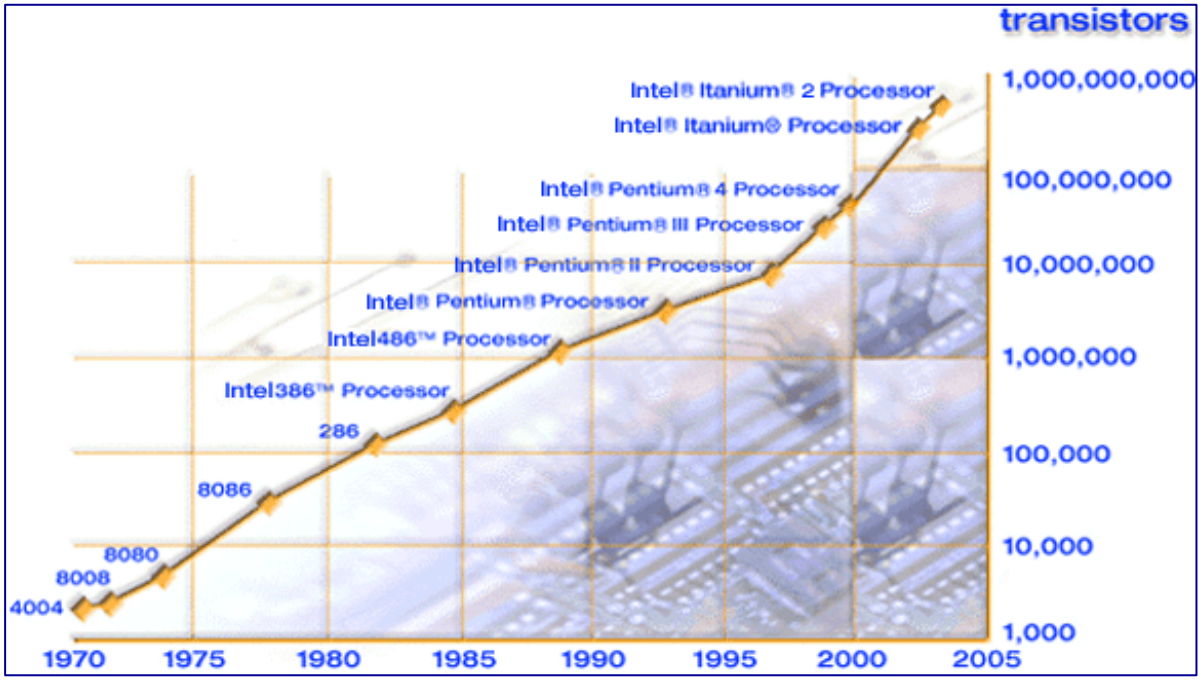
Yuri A. Berlin
Northwestern University, Department of Chemistry,
Evanston, IL 60208-3113, USA

Moor's Law

The number of transistors per square inch on integrated circuits had doubled every year since their invention.



Gordon E. Moore
Intel co-founder



"Gramming more components onto Integrated Circuits"
Author: Gordon E. Moor
Publication: Electronics, April 19, 1965

Top-down and Bottom-up Approaches

Top-down

Creating nano-scale object by physically or chemically breaking down macro materials

Examples: photo-, ion beam-, electron- or X-ray-lithography.

Bottom-up

Assembling nano-scale object atom-by-atom or molecule-by-molecule (self-assembling)

Example: DNA-based molecular construct.

What Approach is Accesible to Ionizing Radiation?

The short answer is both.

Prof. Jacqueline Belloni, CNRS-UPS

Top-down approach, for example, was used for radiation-induced synthesis of monodisperse nanoclusters and bimetalic clusters alloyed or segregated in core-shell structure.

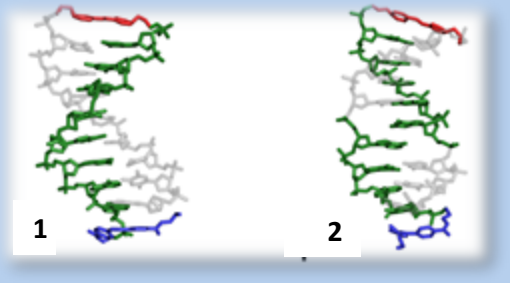
Radiation Chemistry of Nanocolloids and Clusters. BELLONI, J; MOSTAFAVI M. in *Radiation Chemistry: Present status and future trends*, C.D. Jonah and M. Rao, Eds, Elsevier, **2001**, 411-452.

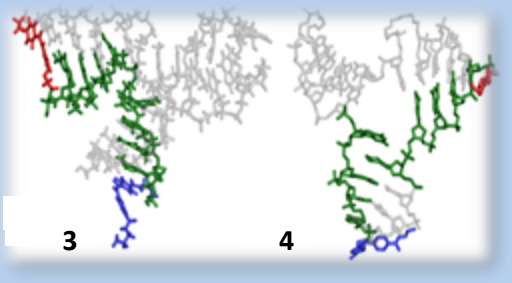
Dr. John Warman, TU-Delft

Bottom-up approach becomes accesible to ionizing radiation since J. Warman proposed the pulse radiolysis time-resolved microwave conductivity technique to generate charge carriers on isolated polymer chains.

Hoofman, R. J. O. M.; de Haas, M. P.; Siebbeles, L. D. A.; Warman, J. M. *Nature* **1998**, *392*, 54-56.

Outline



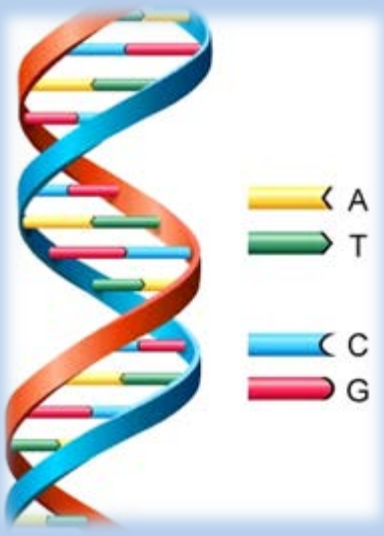


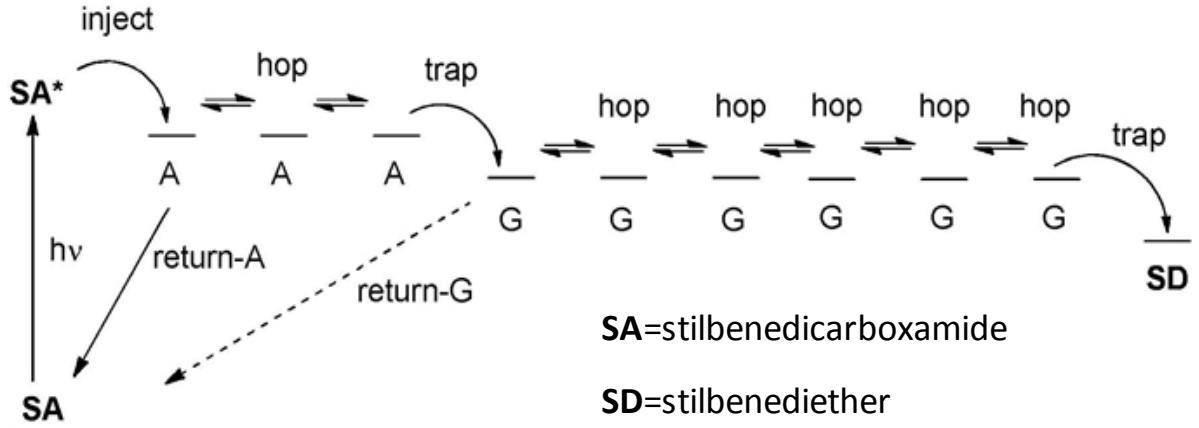
- Short overview of results obtained for one-dimensional charge transport in DNA duplexes

  For review, see e. g. Berlin, Y. A.; Burin, A. L.; Ratner, M.A. *J. Am. Chem. Soc.*, **2001**, *123*, 260; Berlin, Y. A.; Kurnikov I. V.; Beratan, D. *Top. Curr. Chem*. **2004**, *237*, 1.

- Some DNA-based elements of molecular curcuits: connectors and splitters/combiners of charge flow
- Molecular structures promising for the design of splitters/combiners: DNA-based three-way junctions.
- Charge propagation across these junctions
- Dynamics of DNA-based three-way junctions
- Electron coupling and stacked geometries of junctions with linkers.
- Stabilization of their T-form conformations by linker groups
- DNA-based splitters/combiners for charge flow

One-dimensional Charge Motion in DNA Duplexes

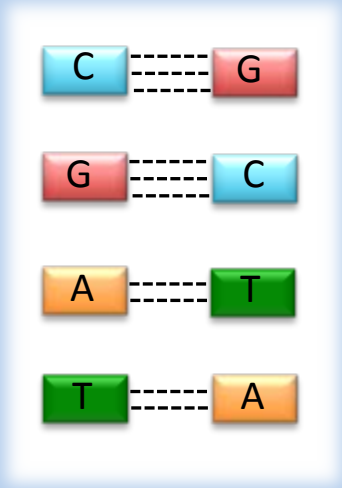




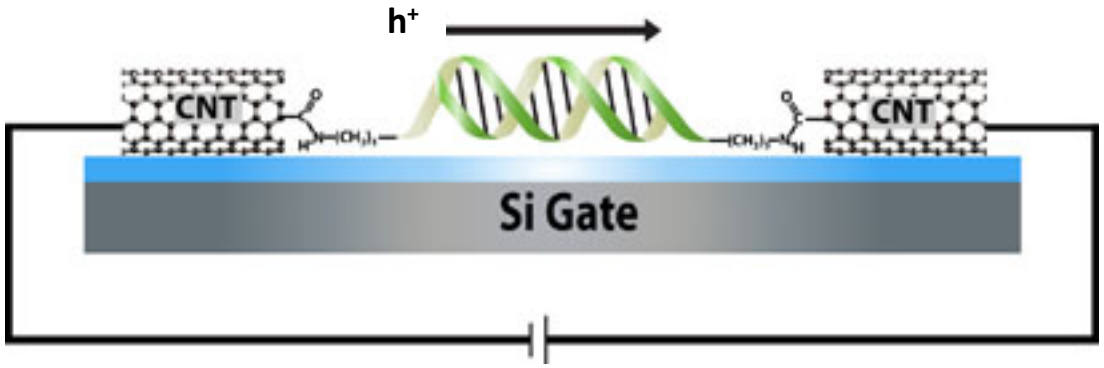
SA=stilbenedicarboxamide

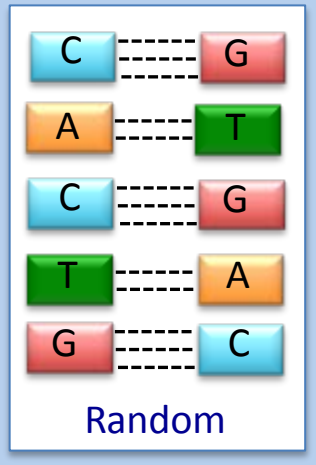
SD=stilbenediether

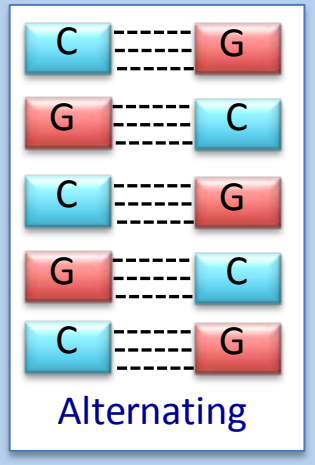
Without G-block tunneling through up to 3 bases will dominate.

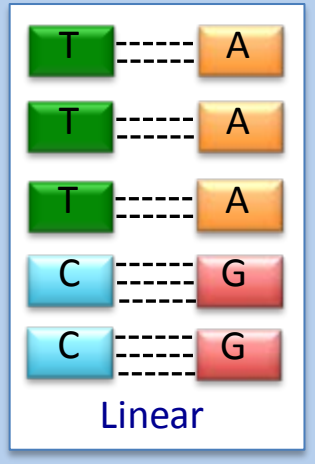


These one-dimensional DNA wires can serve as connectors between elements of molecular circuits.









Main Results for One-dimensional DNA Duplexes

- Charge can travel quite large distances (≅300Å) via sequential hopping

- Efficiency of charge transport depends on sequence. Hole transport through linear poly(purine) DNA sequences has been shown to be more efficient than along random or alternating base pair sequences.

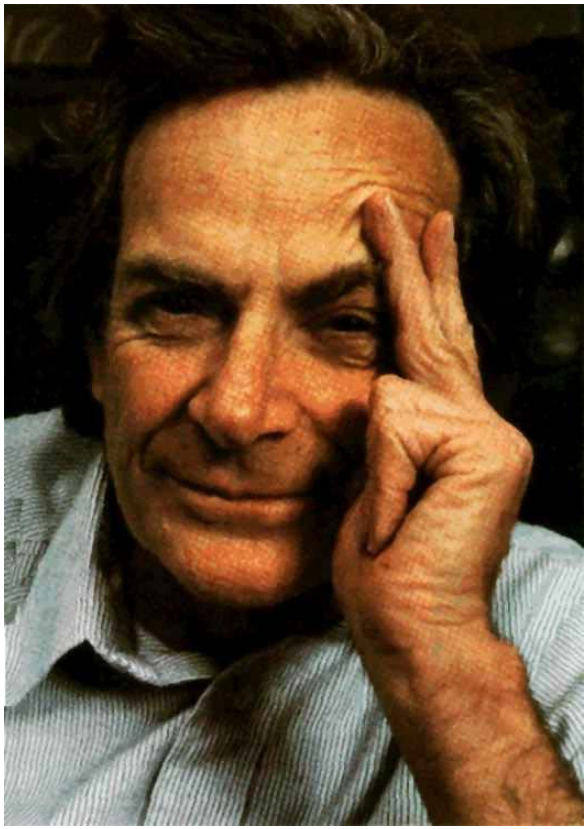
  Lewis, F. D. *Isr. J. Chem*. 2**013**, *53*, 350

  Therefore the flow of charge in a DNA-based assembly can be preferentially guided by rational design.

- Hole motion can be affected by fluctuations in stack geometry and in many cases transport can be treated as conformationally gated.

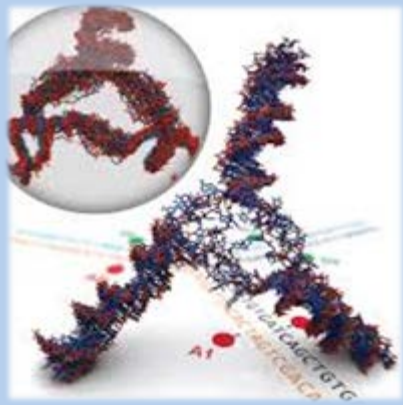
  Grozema, F. C.; Tonzani, S.; Berlin, Y. A. et al. *J. Am. Chem. Soc.* **2008**, *130*, 5157

  Woiczikowski, P. B.; Kubař, T.; Gutiérrez, R. et al. *J. Chem. Phys.* **2009**, *130*.



"What I cannot create, I do not understand. "

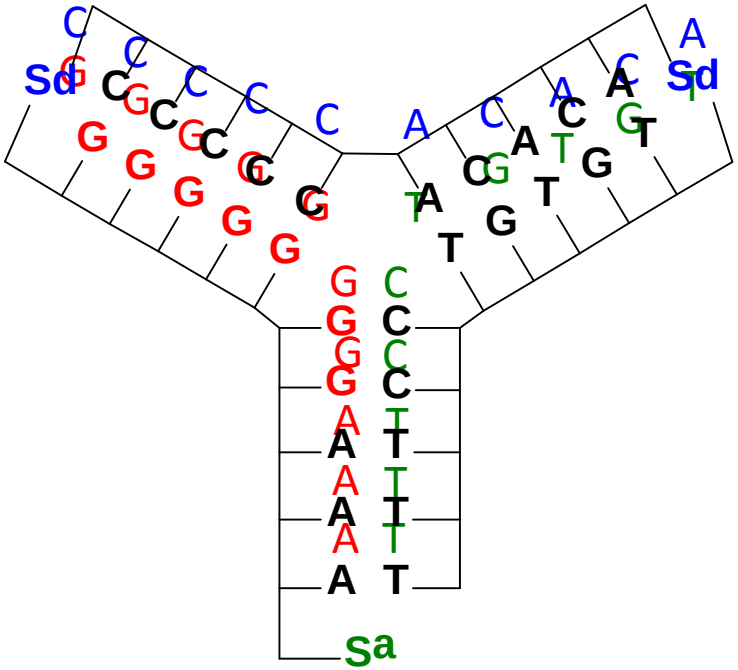
Richard Feynman



Higher Elements of Molecular Circuits: DNA-Based Molecular Junctions

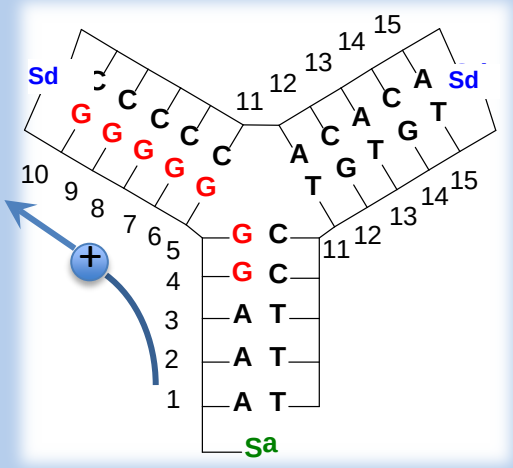
The First Generation of DNA Three-Way Junctions (TWJs)

Young, R.M. et al *J. Am. Chem. Soc.* **2015**, *137*, 5113.

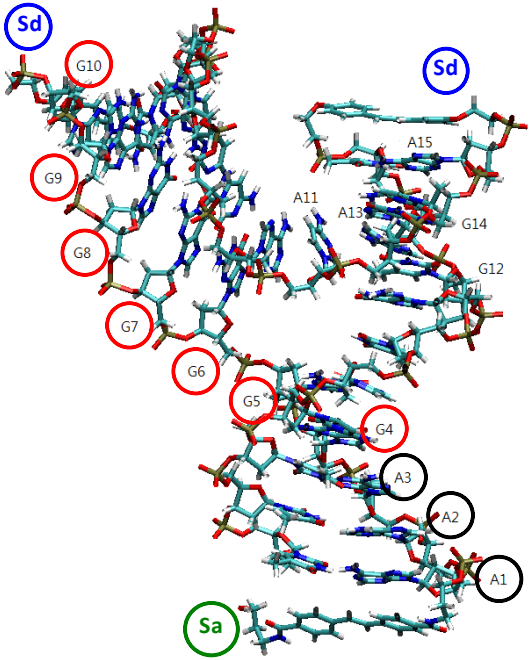


These branched systems can (i) change the direction of the current flow and (ii) serve as molecular splitters/combiners!

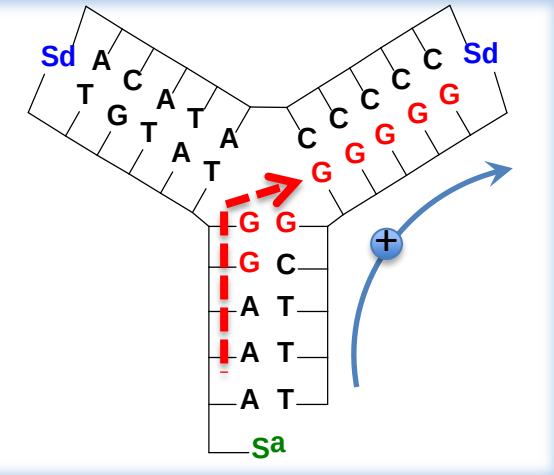
Molecular Structure of DNA-Based Three-Way Junctions



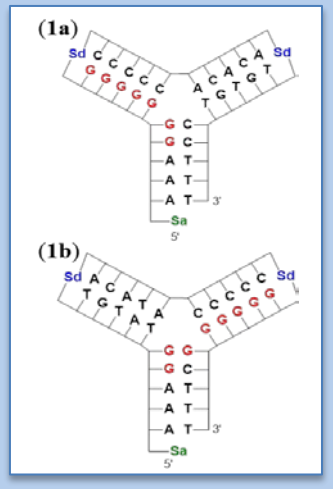
Combination of extended MD simulations (up to 20 ns), the k-means data analysis and quantum mechanical calculation of parameters controlling charge transfer enables one to reveal molecular structure of the first-generation DNA-based TWJs

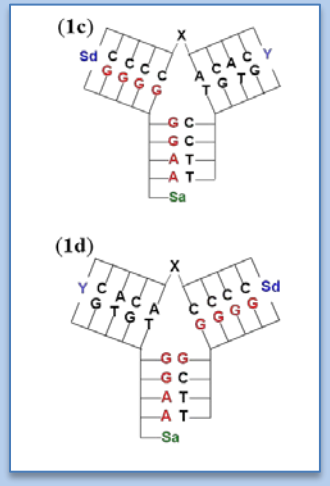


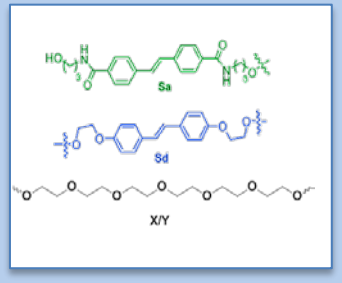
Both theory and experiment demonstrate that hole flow passes from Sa to Sd through the pathway formed by polypurine strand. However splitting of charge flow is small.



Can we increase splitting?







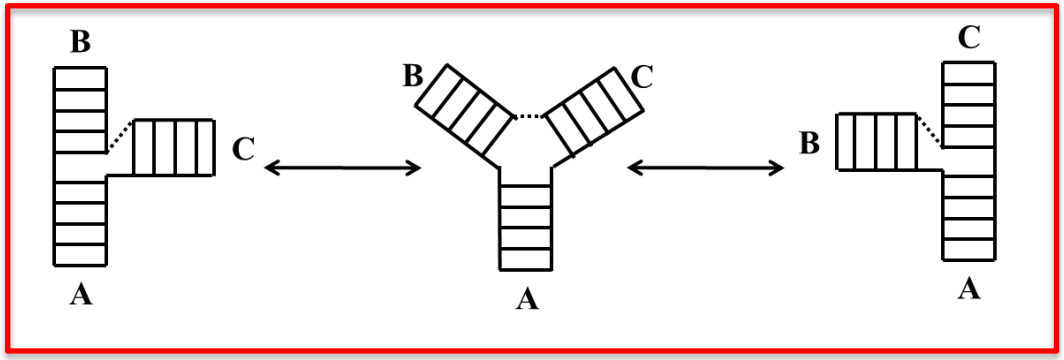
Charge propagation across DNA-Based TWJs

Analysis of electronic couplings calculated for neighboring bases shows that

- within the same branch this parameter is about 0.8 eV, i. e. similar to the value in B-DNA;
- couplings between bases in different branches ("cross-junction" couplings) depend on the structure of the junction;

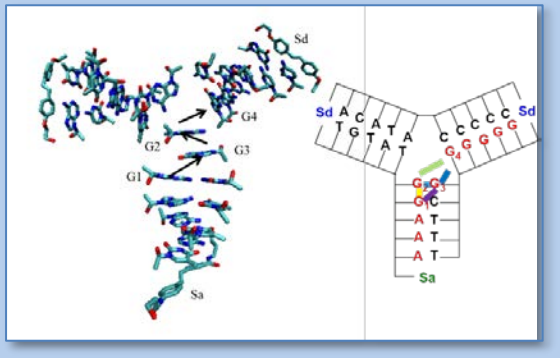
MD simulations demonstrate that on nanosecond time scale

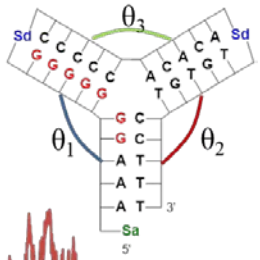
- structure of the junction is strongly affected by conformational fluctuations and therefore charge transport in TWJ may involve gated charge hopping
- two of the three DNA strands can form a B-DNA like stack, while the third branch can be located nearly perpendicular to the stack, thus shaping a "T" form

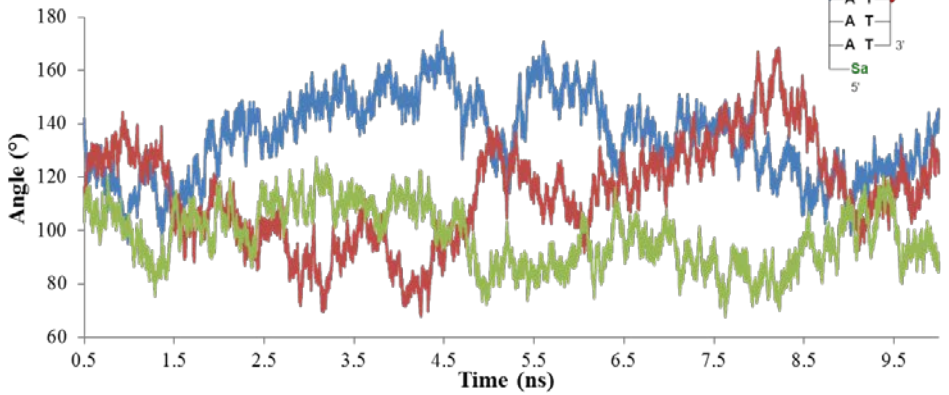


DNA TWJs without linkers: Rapid Switches between Conformations

"T" conformation is characterized by having one of the angles equals to ~ 180°. In this TWJ structure, interconversion among the T-conformations proceeds in 1-3 ns.







Dynamics of new pathway formation

Phase 1. Duration is the first 2 ns. All Gs are paired. Bases G_1 and G_2 exhibit the strongest coupling.

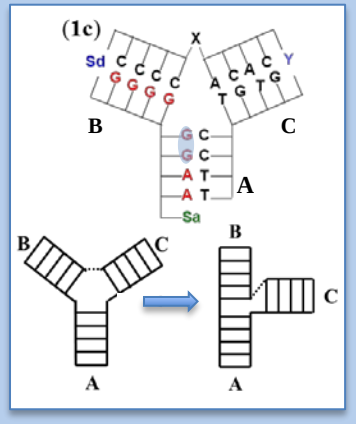
Phase 2. Duration is from 2 till 10 ns. The coupling between mismatched bases G_2 – G_3 breaks. Strong interaction between G_1 and G_3 arises.

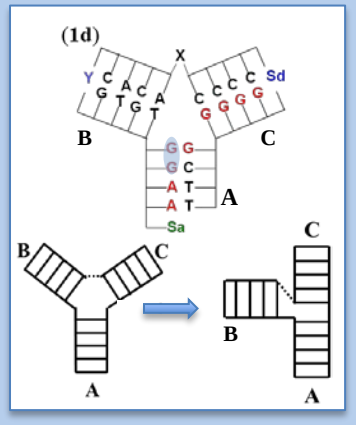
Phase 3. Duration from 10 till 12 ns. Fluctuations bring G_2 and G_4 in close proximity, enhancing their coupling.

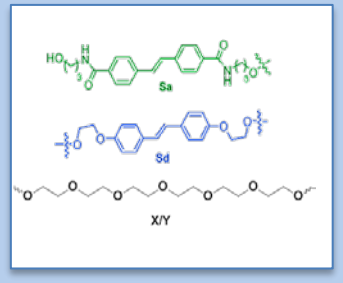
Phase 4. Duration from 12 till 15 ns. Cross-junction interaction becomes weak, and the G_2-G_3 bases form a pair again.

Thus a new pathway $G_1 \rightarrow G_3 \rightarrow G_2 \rightarrow G_4$ is activated to cross the junction.

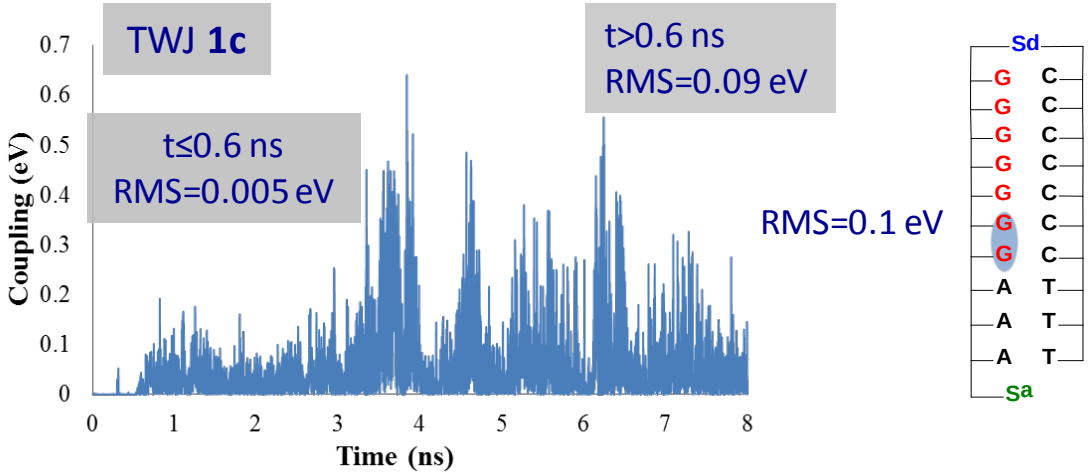
DNA TWJ with a Linker: Stabilizing "T" Conformations





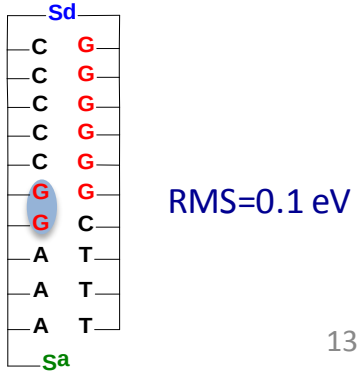


To stabilize "T" conformations polyethylene glycol (PEG) linking group was used. The incorporation of PEG at TWJ is intended to add flexibility and thus increase stacking of purine bases.

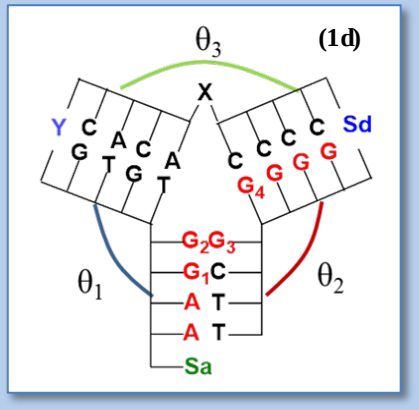


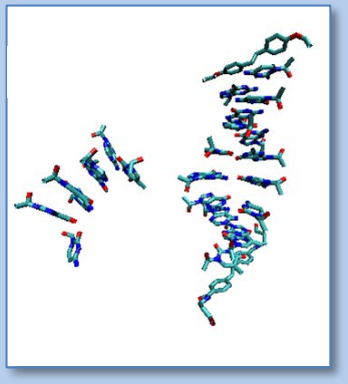
Similarly, RMS=0.005 eV for G_1-G_2 coupling in TWJ **1d** during the first 1.7 ns and thereafter increases up to 0.1 eV.

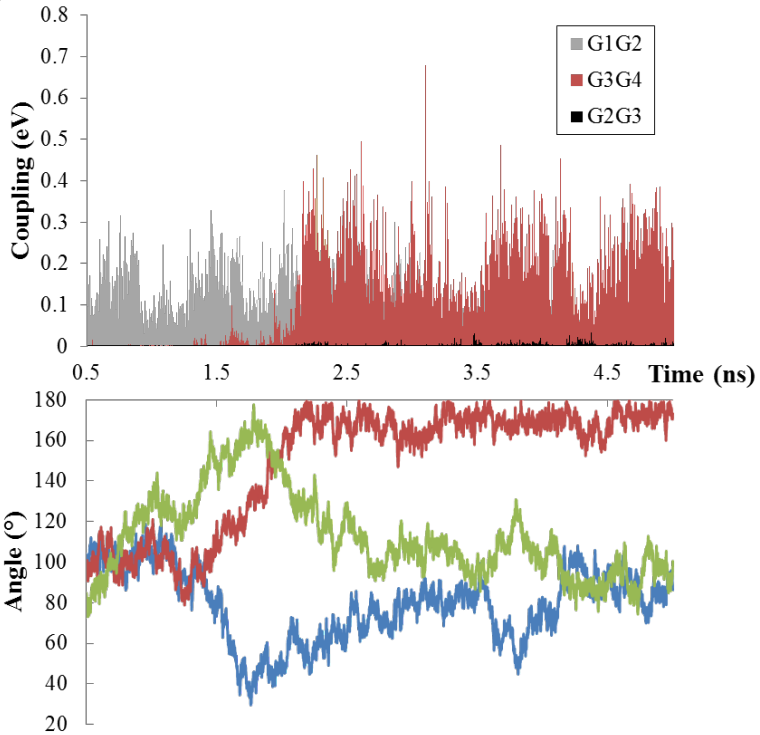
In both cases RMS of couplings in stacked geometry of TWJ and in B-DNA oligomer with the same sequence almost coincides. This suggests that at t>0.6 ns TWJ with a linker is locked in "T" conformation



Dynamics of DNA TWJ with a Linker and Stabilization of "T" Conformations

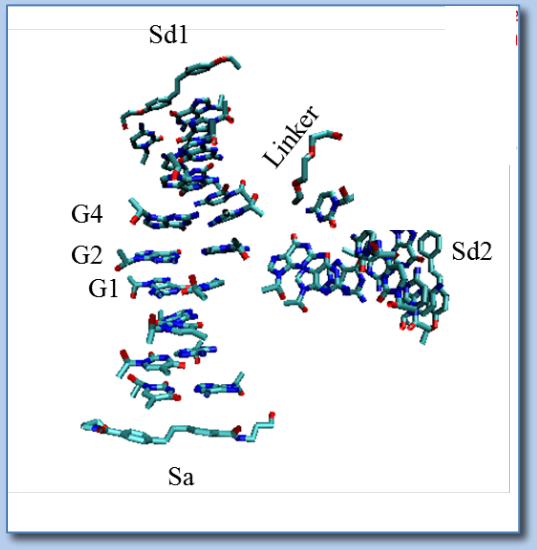


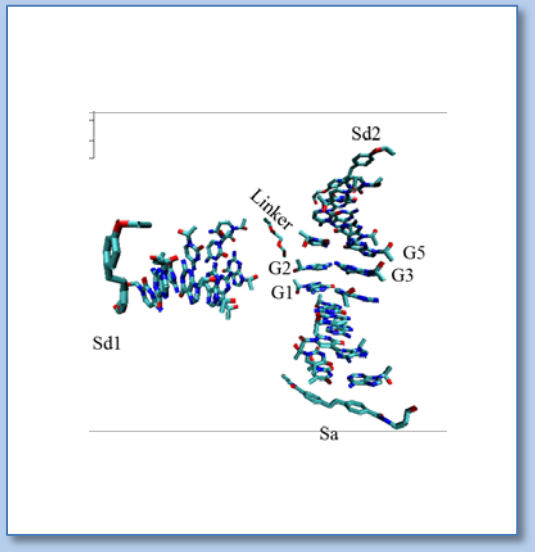




Once the π-stacked geometries form, the cross-junction coupling is strongly enhanced. This TWJ is locked in the T-shaped geometry after ~2 ns.

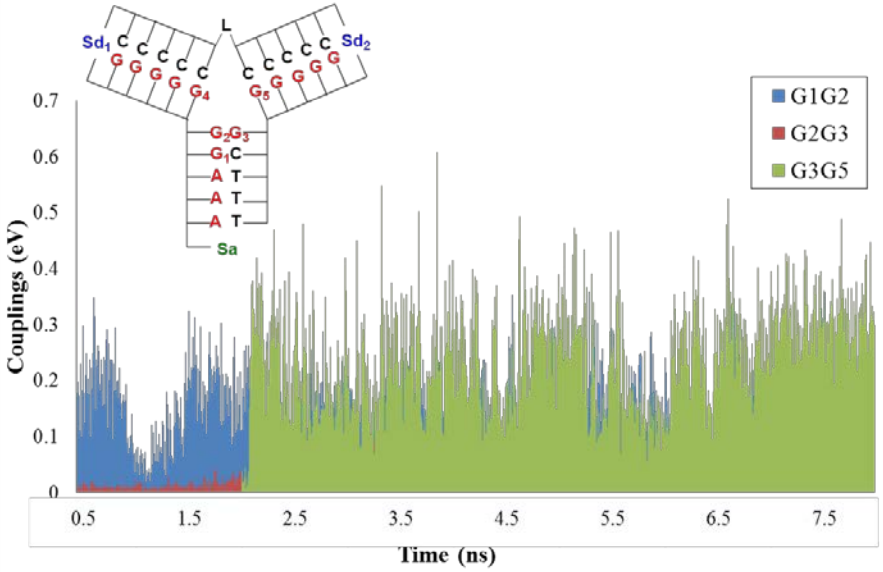
DNA TWJ Splitter/Combiner for Charge Flow





In the MD simulations, stable "T" shaped conformations appeared after several nanoseconds and their structures are locked for 25 ns.

Due to symmetry, these conformations allow charge to penetrate into both upper arms, thus making DNA TWJ appropriate for splitting of charge flow



For the lower "T" configuration, RMS coupling G2-G3 is 0.018 eV (the slowest step), while for the upper "T" shaped conformation, RMS couplings for all steps remain almost the same and are equal to 0.1 eV (as in B-DNA)

The ratio of charge flows to the upper-left (I_L) to the upper-right (I_R) arms (the so-called splitting ratio) is 25 because of the weaker coupling in the right arm.

Conclusions

- Simulated DNA TWJs are found to fluctuate among "T" structures. The coupling across the junctions is enhanced when a "T" structure exhibits B-DNA like π-stacking. This is found in the simulations only when PEG linkers are embedded in DNA. Indeed, the more poorly stacked structures have nearest-neighbor couplings several orders of magnitude weaker than in B-DNA. These simulations are consistent with measured CT rate and yield data.

- Structures without a linker are found to undergo rapid switching between different "T" conformations. Even while in "T" conformations, the "cross-junction" couplings in this first generation TWJs **are several orders of magnitudes smaller than the nearest-neighbor couplings in B-DNA**. Structures of DNA TWJs with PEG linkers are locked into well-stacked "T" conformations, where **the "cross-junction" couplings are similar to the nearest-neighbor couplings in B-DNA**. As a result, the PEG linked structures should have CT kinetics similar to that found in B-DNA with a corresponding purine pathway.

- We also explored the charge transport pathways in a possible DNA TWJ charge splitter/combiner of the charge flow. The simulations indicate that charge can indeed proceed to both of the upper arms of the TWJ, thus suggesting that DNA-based splitter/combiners should be within reach.

Acknowledgement

The author thanks the Office of Naval Research for financial support (MURI grant N00014-11-1-0729). He also appreciate computer resources provided by the National e-Science Infrastructure Consortium for this project (URL: http://www.e-science.in.th). The author is grateful to the following members of the MURI team for helpful discussions and for scientific collaboration.

David Beratan

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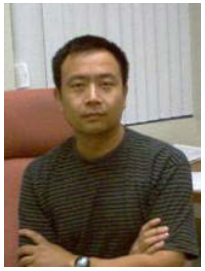

Nongjian Tao

Ned Seeman

Ferdinand Grozema