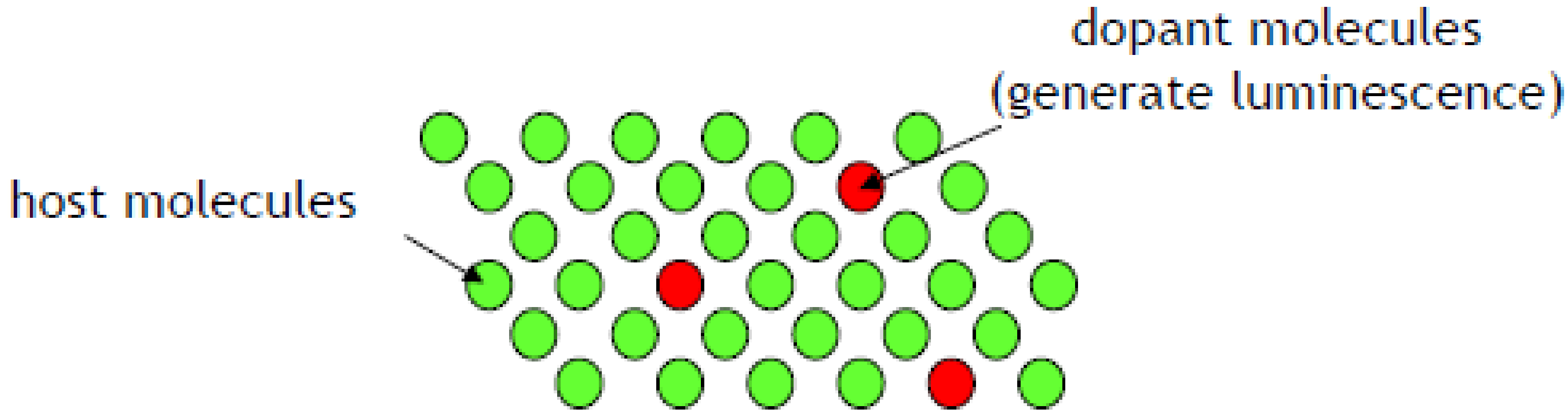
Organic semiconductors: energy, charge transfer, and research frontier

PH 673

Nanoscience and nanotechnology

November 14, 2025

Nonradiative Energy Transfer



How does an exciton in the host transfer to the dopant?

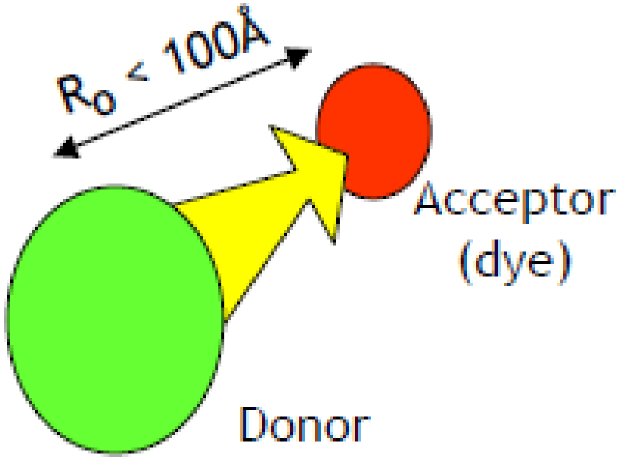
Two possible energy transfer processes:

1. Förster transfer

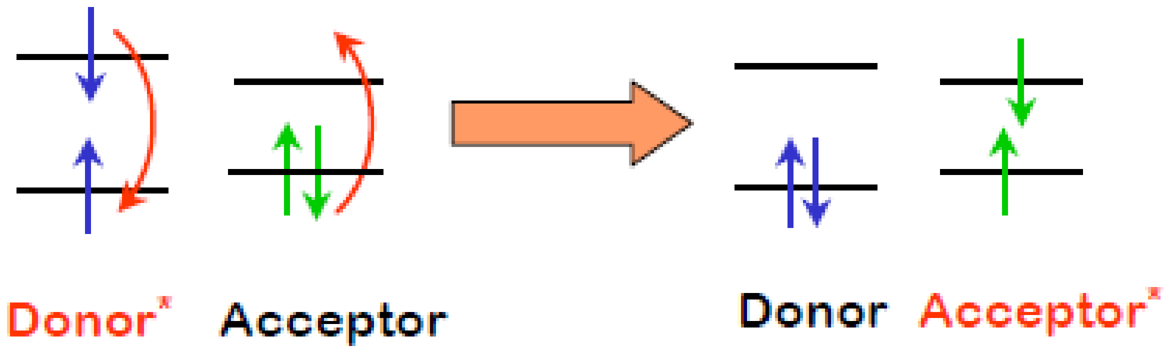
2. Dexter transfer

Förster transfer

- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed



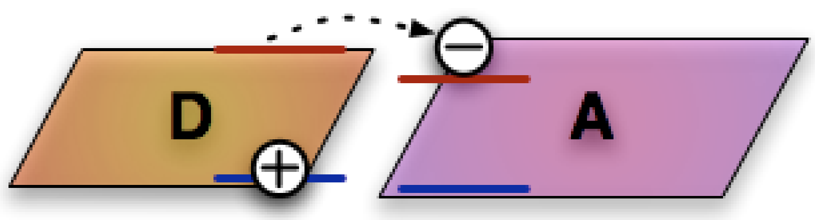
very fast <10^{-9}s



only singlet excitons participate

D-A Systems

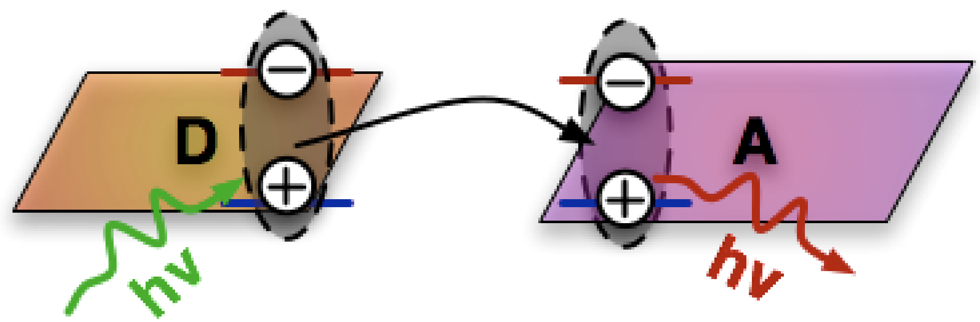
Charge Transfer



Donor-Acceptor system can facilitate exciton dissociation via charge transfer

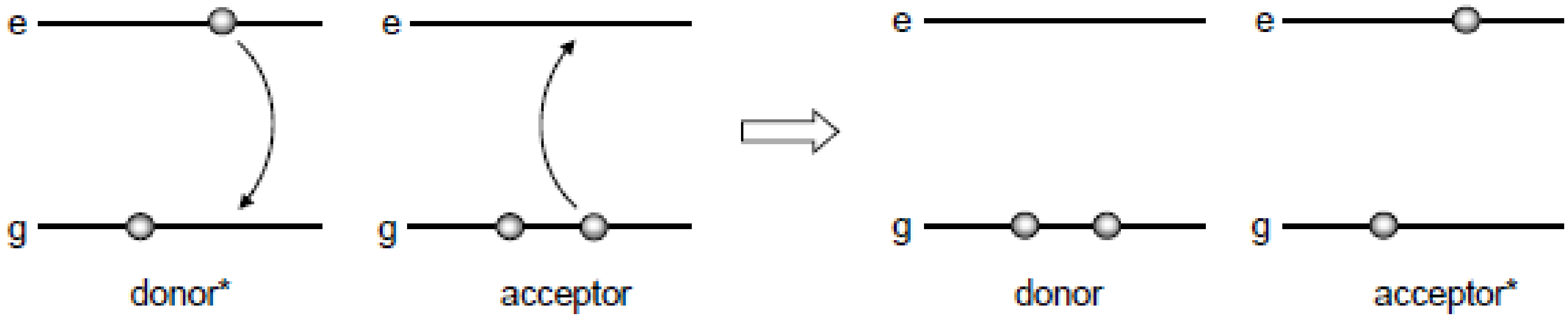
Energy Transfer

Competing process: energy transfer (e.g. Förster Resonant Energy Transfer (FRET))



Need to know under what conditions charge or energy transfer dominates

D-A interactions: energy transfer



$$\Psi_i = \psi_D^u \psi_A \qquad \Psi_f = \psi_D \psi_A^u$$

$$|H_{DA}| = \int \Psi_f V_{DA} \Psi_i dr = \int \psi_D \psi_A^u V_{DA} \psi_D^u \psi_A dr$$

$$V_{DA} = \mathbf{E}_D \cdot \boldsymbol{\mu}_A = \frac{\boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A}{4\pi\varepsilon_0 r^3}$$

$$\Gamma_{DA} = \frac{\pi}{2\hbar^2} |H_{DA}|^2 \delta(\omega_D - \omega_A)$$

$$V_{DA} \propto \frac{\kappa \mu_D \mu_A}{r^3}$$

$$\Gamma_{DA} \propto \frac{\kappa^2}{r^6} \left| \int \psi_D \mu_D \psi_D^u dr_D \right|^2 \left| \int \psi_A^u \mu_A \psi_A dr_A \right|^2 \delta(\omega_D - \omega_A)$$

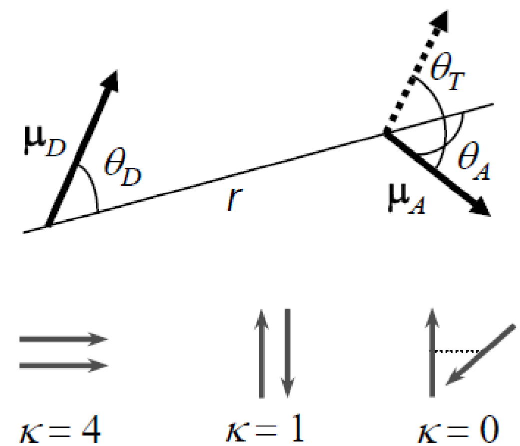
D-A interactions: energy transfer

$$\Gamma_{DA} = \frac{\pi}{2\hbar^2}\left|H_{DA}\right|^2 \delta(\omega_D - \omega_A)$$

$$V_{DA} \propto \frac{\kappa \mu_D \mu_A}{r^3}$$

$$\Gamma_{DA} \propto \frac{\kappa^2}{r^6}\left|\int \psi_D \mu_D \psi_D^u dr_D\right|^2 \left|\int \psi_A^u \mu_A \psi_A dr_A\right|^2 \delta(\omega_D - \omega_A)$$

$$\kappa = \cos\theta_T - 3\cos\theta_D \cos\theta_A$$



$$\Gamma_{DA} \propto \frac{\kappa^2 \phi_F}{r^6 \tau_F}\int_0^\infty \varepsilon_A(\omega)\overline{F}_D(\omega)\omega^{-4} d\omega$$

D lifetime

Absorption of A

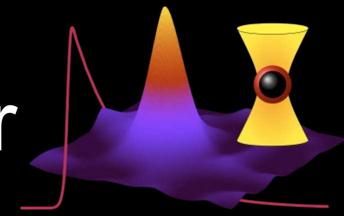
Fluorescence of D

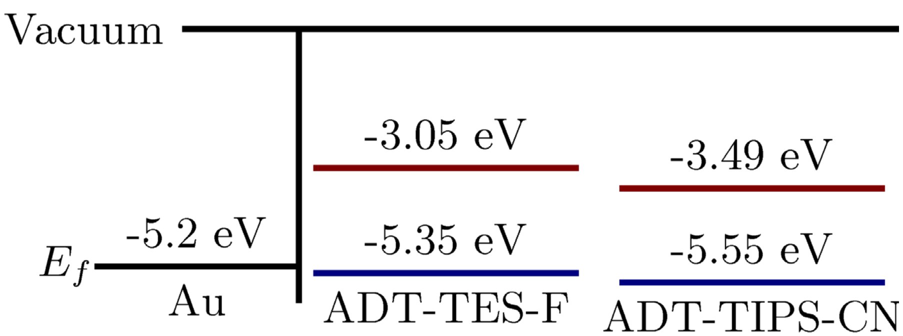
$$\Gamma_{DA} = \frac{1}{\tau_F}\left(\frac{R_0}{r}\right)^6$$

Forster radius

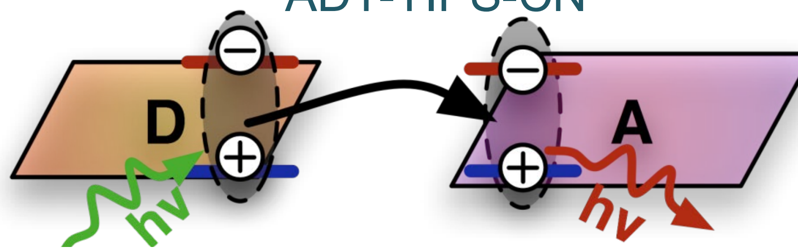
Oregon State UNIVERSITY

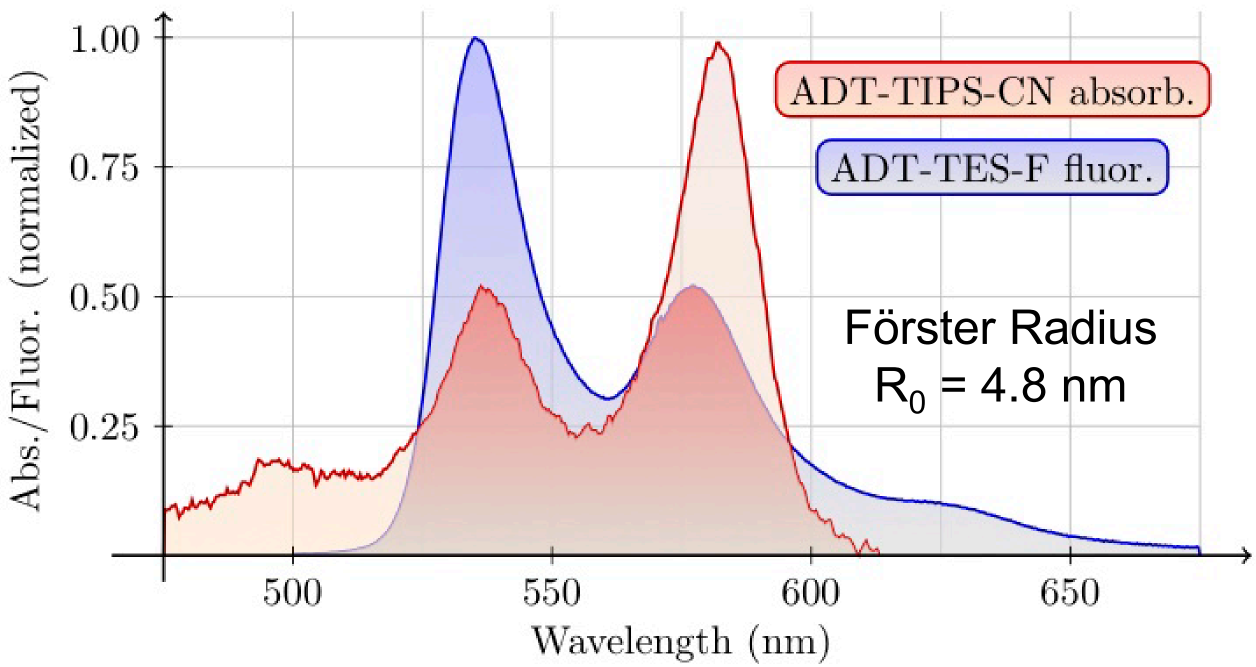
D-A interactions: energy transfer





Strong energy transfer between ADT-TES-F and ADT-TIPS-CN





Förster Radius

R_0 = 4.8 nm

$$R_0^6 = \frac{9\ln(10)}{128\pi^5 N}\frac{\kappa^2\Phi_{\mathrm{pl}}}{n^4}J,$$

$$J = \int_0^\infty F_{\mathrm{d}}(\lambda)\epsilon_{\mathrm{a}}(\lambda)\lambda^4 d\lambda,$$

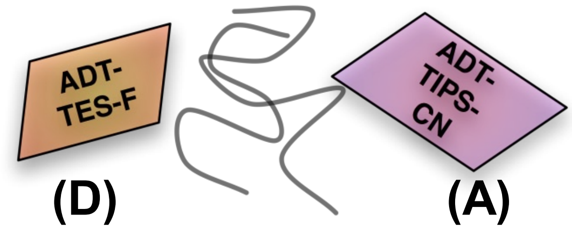
$$E = \frac{1}{1+(r/R_0)^6}$$

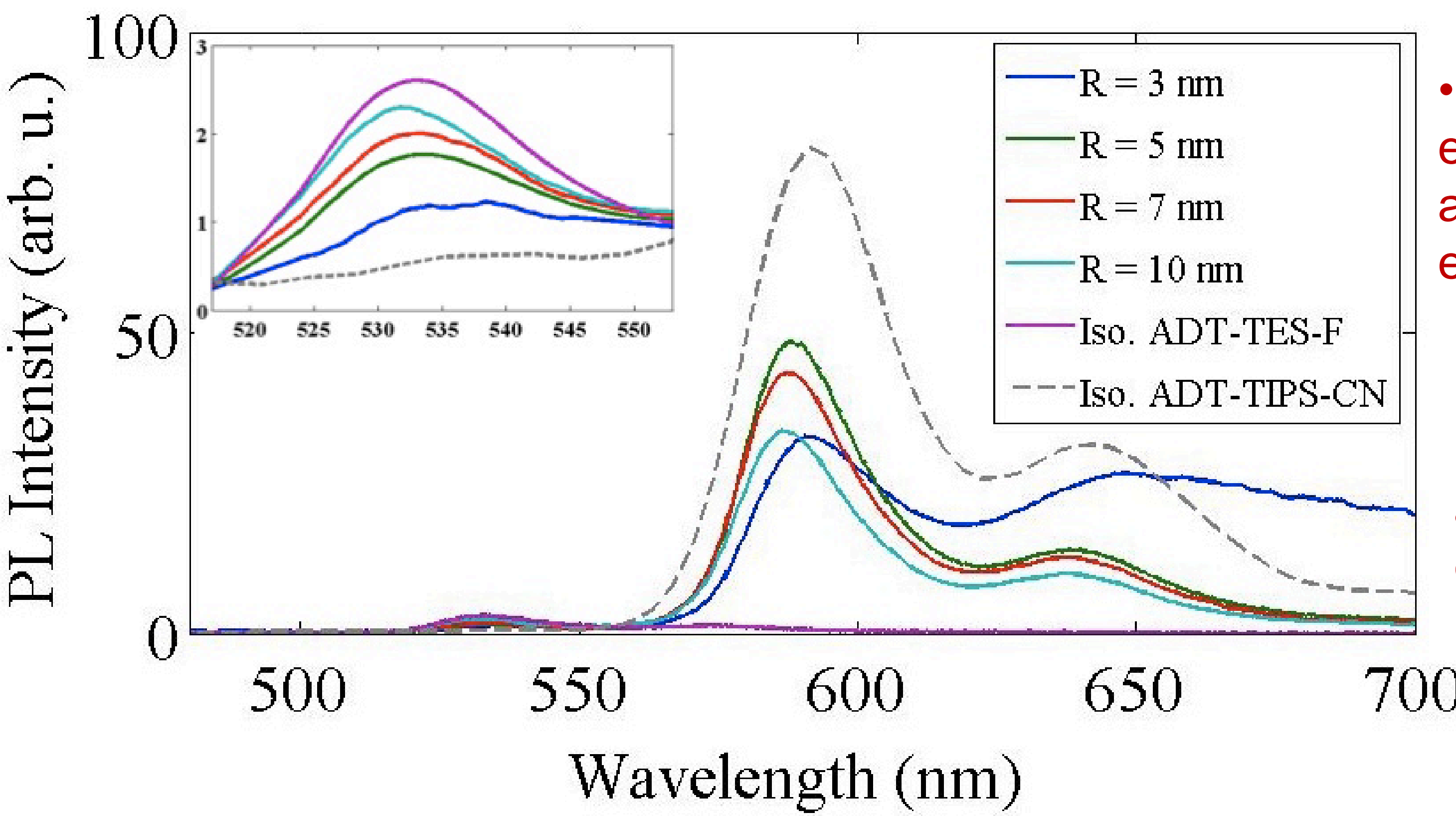
W. E. B. Shepherd *et al. J. Phys. Chem. Lett.* **2,** 362-366 (2011)

A.D. Platt *et al.*, *Proc. of SPIE*, 7413(1), 74130S (2009)

D-A energy transfer in PMMA

Concentrations < 5.9 x 10^{-2} M ➡ additive combinations of donor and acceptor isolated spectra





- Strong enhancement of A and quenching of D emission
- Onset of aggregation is consistent

Shepherd *et al. J. Phys. Chem. Lett.* **2,** 362-366 (2011)

Dexter transfer

diffusion of excitons from donor to acceptor

'Wigner-Witmer spin conservation rules'

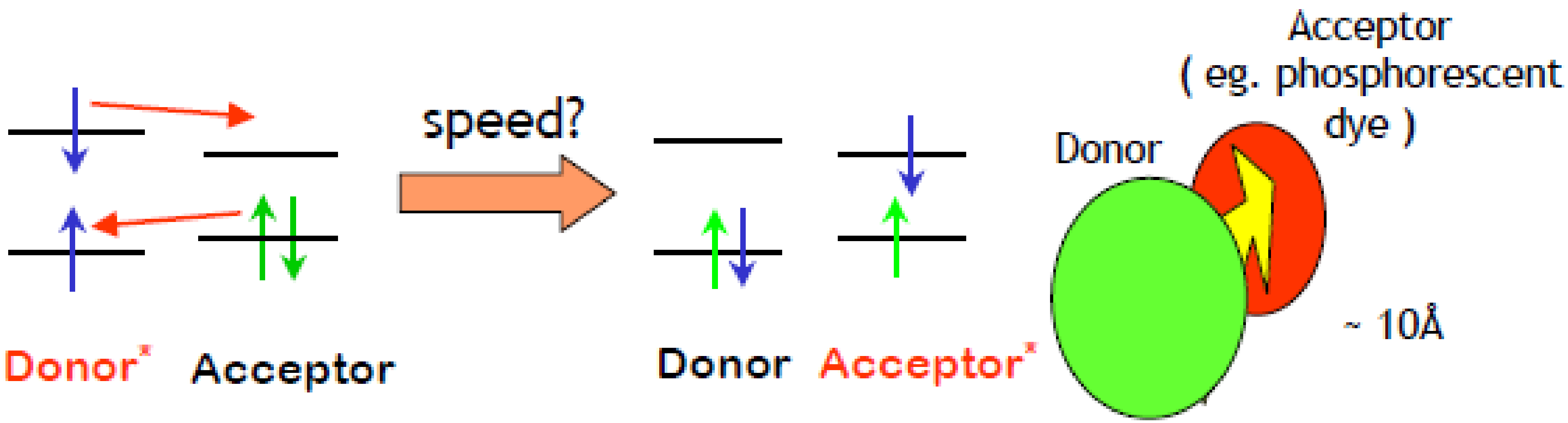
$$A + B \rightarrow C + D$$

total spin of reactants: $(S_A+S_B),(S_A+S_B-1),\ldots,|S_A-S_B|$

total spin of products: $(S_C+S_D),(S_C+S_D-1),\ldots,|S_C-S_D|$

reaction allowed if two sequences have a number in common

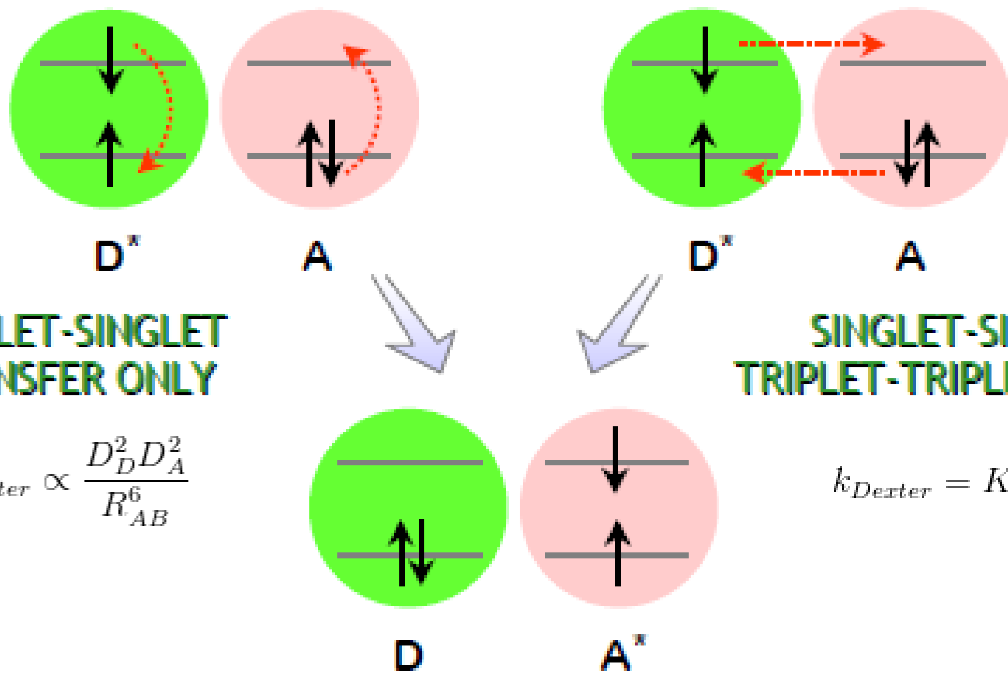
only singlet-singlet, triplet-triplet allowed



Nonradiative Energy Transfer

Förster, Coulombic
(long range ~30-100 Å)

Dexter, e⁻ exchange
(short range ~6-20 Å)



SINGLET-SINGLET TRANSFER ONLY

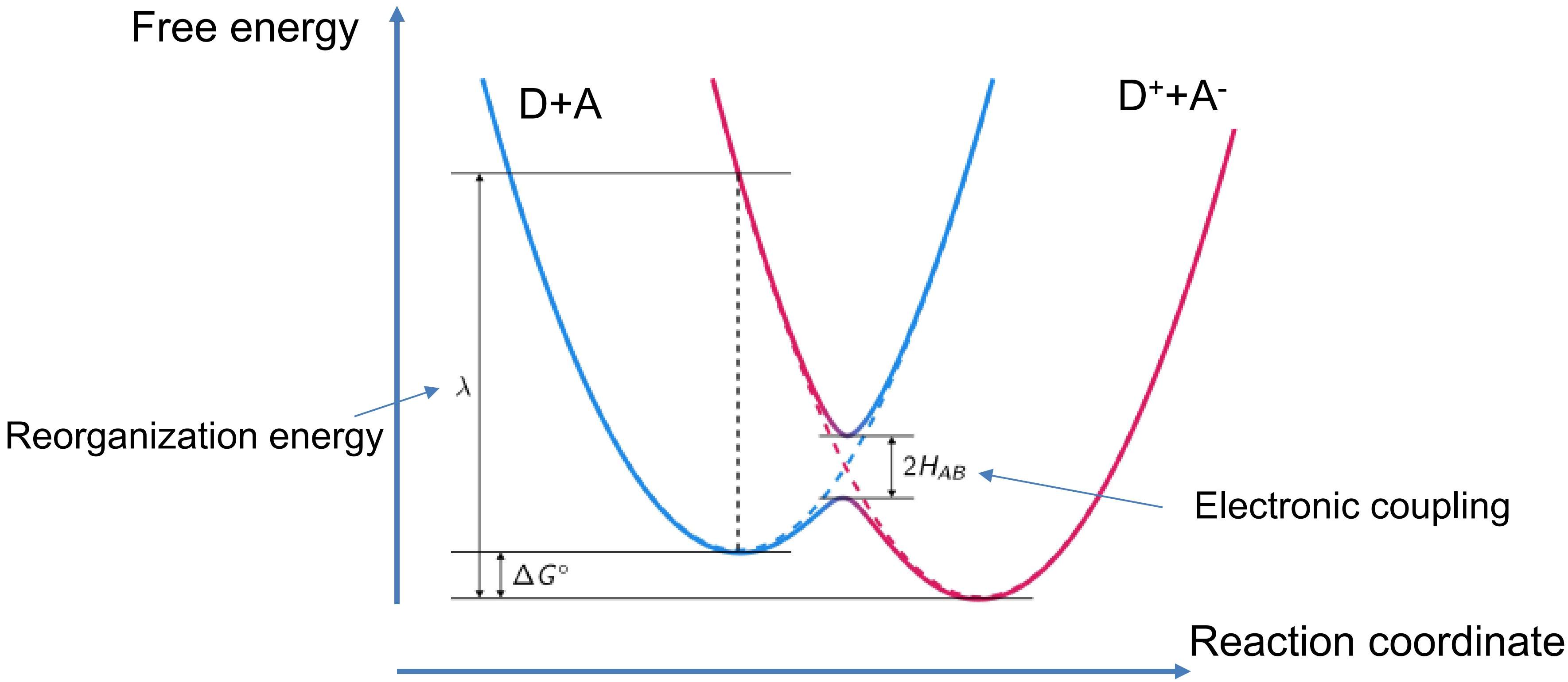
$$k_{Forster} \propto \frac{D_D^2 D_A^2}{R_{AB}^6}$$

SINGLET-SINGLET & TRIPLET-TRIPLET TRANSFER

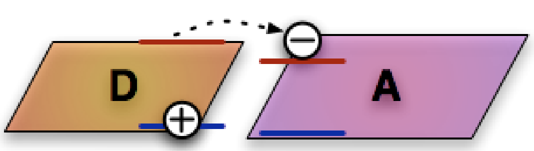
$$k_{Dexter} = KJexp(\frac{-2R_{DA}}{L})$$

Charge transfer

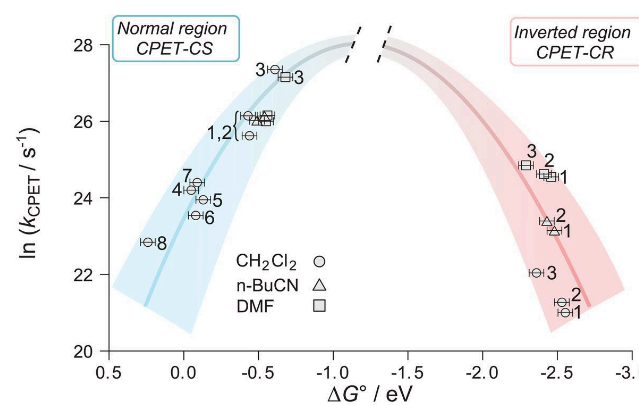
Marcus: Nobel Prize in Chemistry 1992



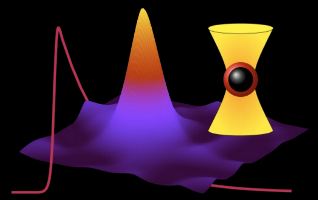
$$k_{et} = \frac{2\pi}{\hbar}|H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_b T}\right)$$



D-A ΔLUMO ~ ΔG



Opportunities for innovation



Innovative molecular structures – use nature-derived sustainable materials

Innovative experimental techniques – measure light-matter interactions with sub-100 fs time resolution

Innovative photophysical processes – singlet fission

Innovative devices – combine electronic and photonic structures

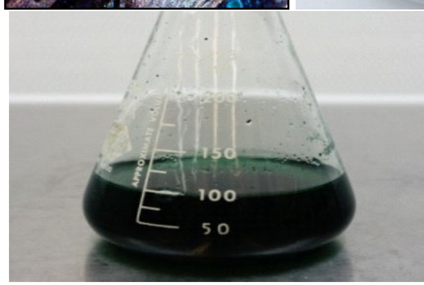
Brief examples of each coming next !

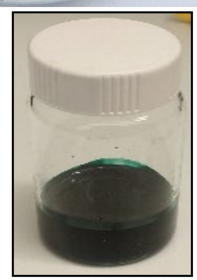
Chlorociboria on decaying wood

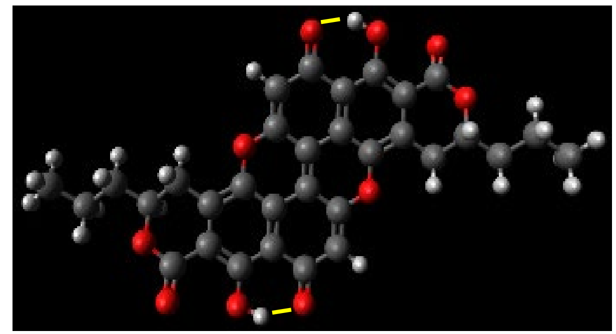
Chlorociboria in nature and art

Sustainable materials: fungi-derived pigme

Oregon-native wood fungi *Chlorociboria aeruginascens* and *Chlorociboria aeruginosa*





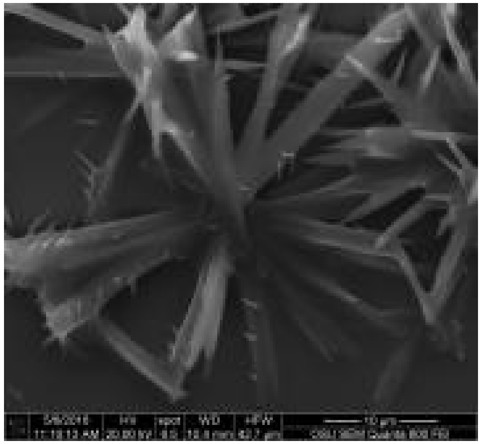


Xylindein

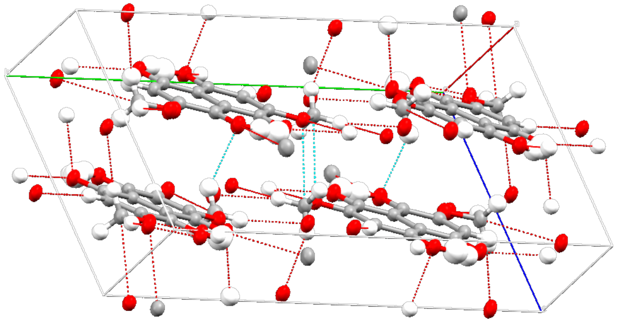
- Broken conjugation
- H-bonding
- Synthesis unsuccessful so far
- Used in art for centuries: ultra-stable
- Nothing was known about optoelectronic properties

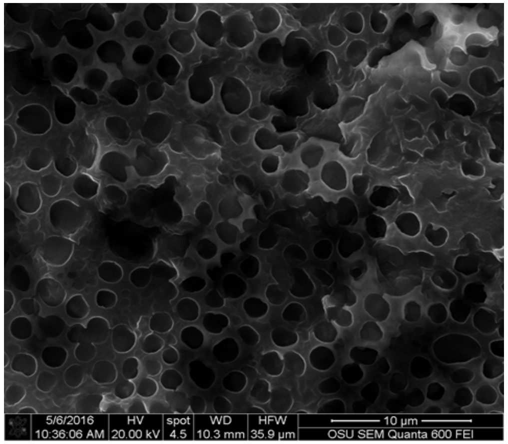
Collaboration with Seri Robinson, OSU Fore
NSF CBET-1705099

Native morphology



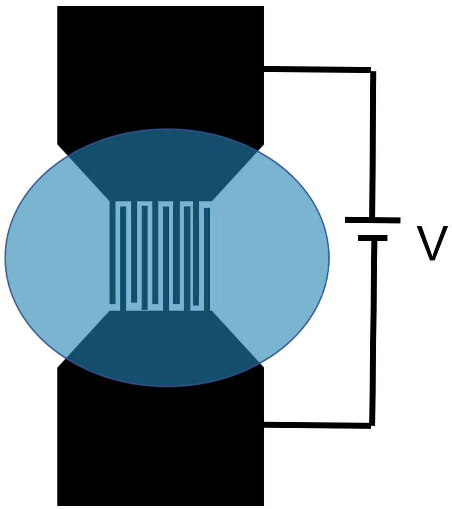
- Crystalline

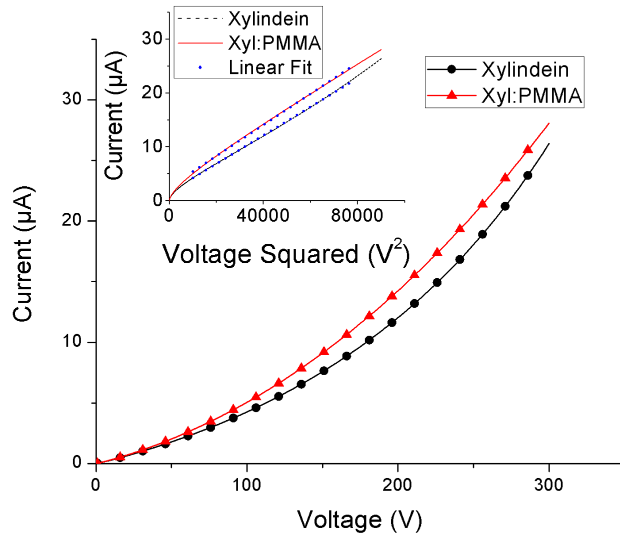


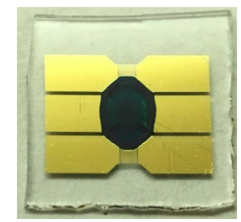


- Amorphous
- Porous

Electrical characteristics



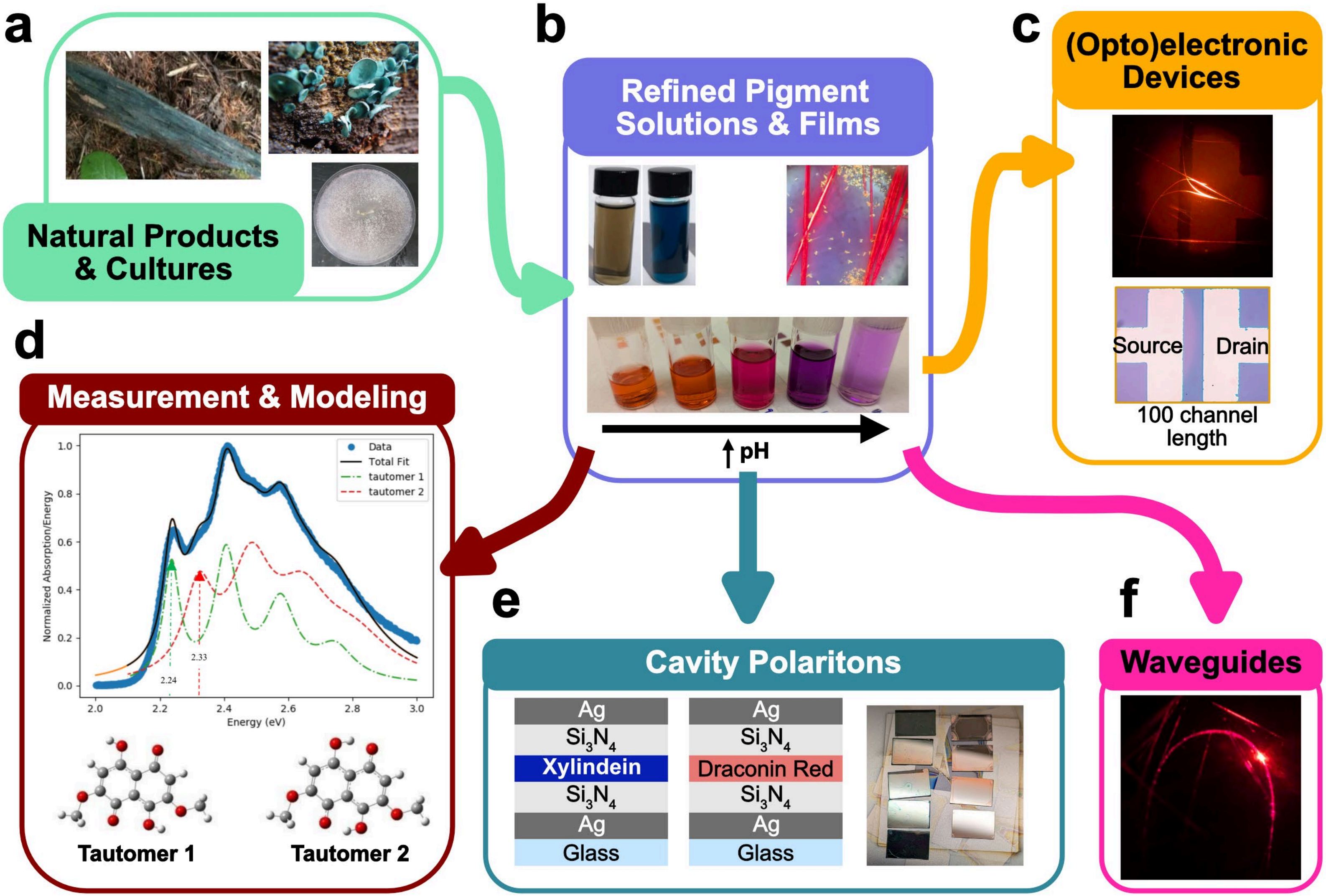




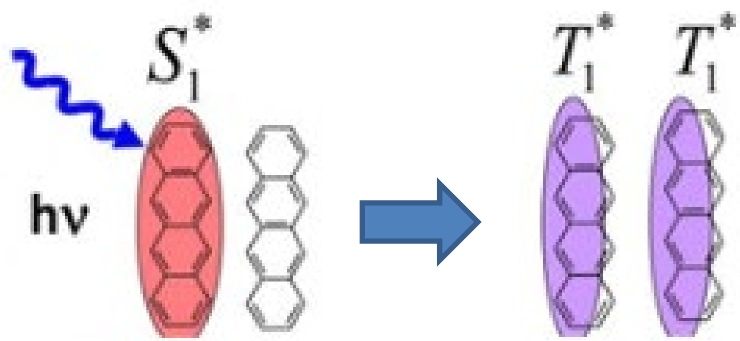
- Xylindein conducts charge carriers !

G. Giesbers, J. Van Schenck, S. Vega Gutierrez, S. Robinson, O. Ostroverkhova, "Fungi-Derived Pigments for Sustainable Organic (Opto)Electronics" *MRS Advances* **3**, 3459 (2018)

Xylindein and Draconin Red as optoelectronic and photonic materials

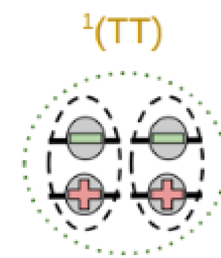


Innovative photophysics: singlet fission



- Excite one molecule (use one photon)
- Excitation redistributes between two molecules – create a "TT" state
- Now have two electron-hole pairs
- Two charge pairs were created by one photon

Use this process to boost power conversion efficiency in solar cells !

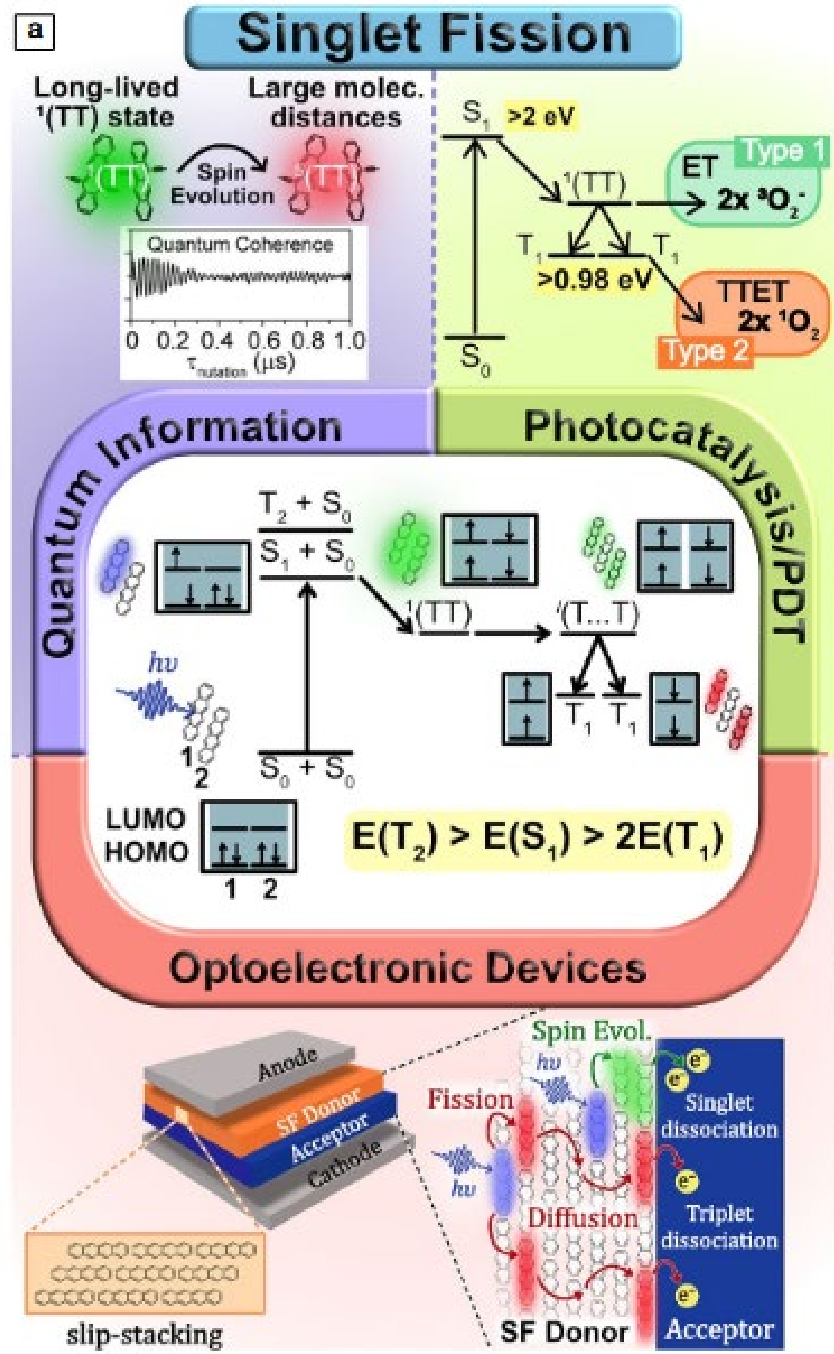


How do we show that we have this process in our materials ?

Time-resolved photoluminescence and pump-probe spectroscopy !

Excitons and polaritons in singlet fission materials: Photophysics, photochemistry, and optoelectronics

Oksana Ostroverkhova,* Winston Goldthwaite, and Roshell Lamug



Singlet fission

$$S_0 + S_1 \longrightarrow T_1 + T_1$$

- Does not require a "spin flip" – unlike ISC (which is "forbidden", and occurs on μs time scales)
- Can occur on fs time scales
- If both triplet excitons can be dissociated into free carriers and collected, get 200% efficiency of charge generation (1 photon in, 2 electrons out)
- Equivalent of impact ionization in inorganic semiconductors

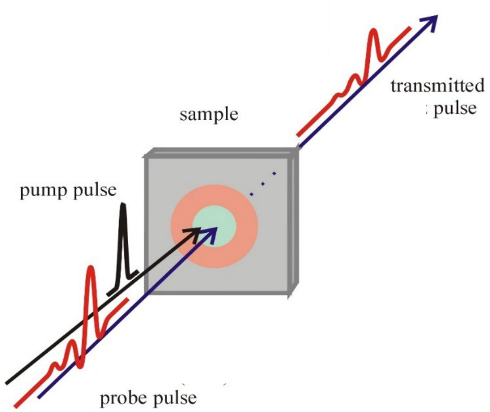
Observing the Multiexciton State in Singlet Fission and Ensuing Ultrafast Multielectron Transfer

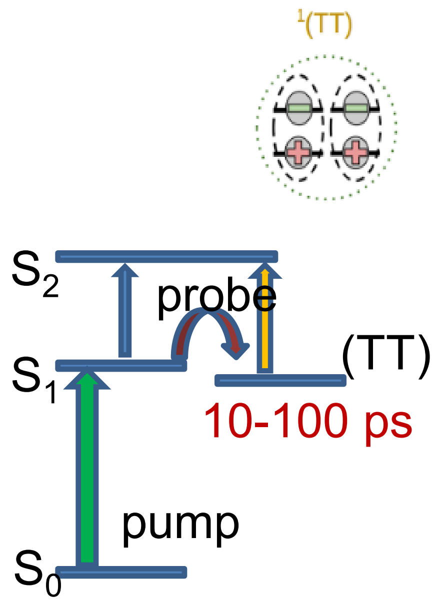
Wai-Lun Chan, Manuel Ligges, Askat Jailaubekov, Loren Kaake, Luis Miaja-Avila, X.-Y. Zhu*

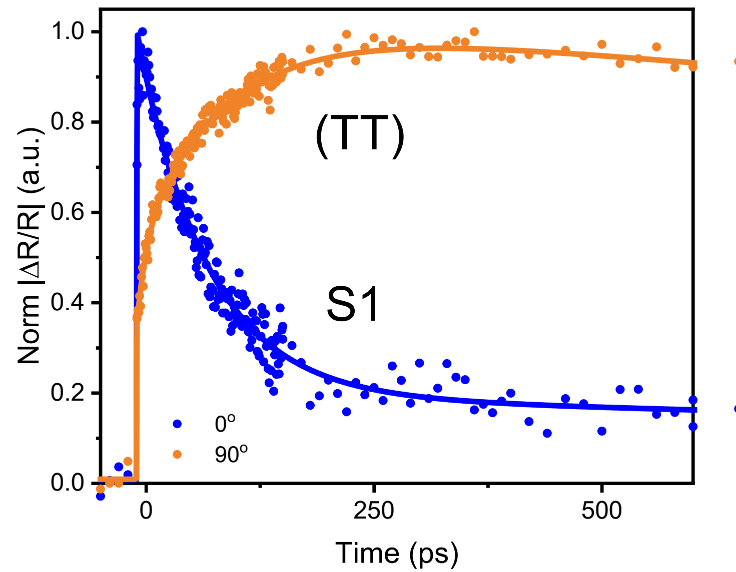
SCIENCE VOL 334 16 DECEMBER 2011 1541

Singlet fission probing

Pump-probe experiments (collaboration with Matt Graham)





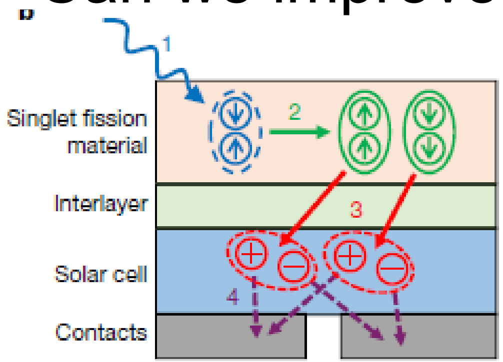


- TT forms on picosecond time scales
- Temperature- and magnetic field-dependent dynamics

G. Mayonado, K. Vogt, J. Van Schenck, L. Zhu, G. Fregoso, J. Anthony, O. Ostroverkhova, M. Graham, "High-Symmetry Anthradithiophene Molecular Packing Motifs Promote Thermally Activated Singlet Fission" *J. Phys. Chem. C* **126** , 4433-4445 (2022) Special issue: Quantum Coherent Phenomena in Energy Harvesting and Storage

Singlet fission in devices

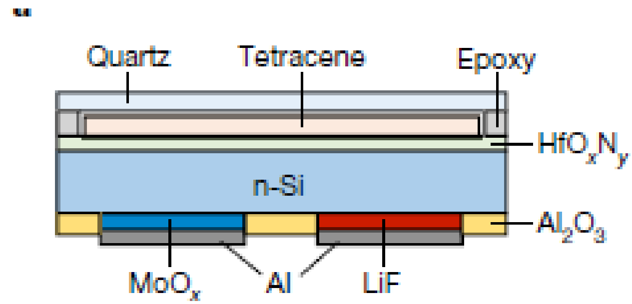
Can we improve Si solar cell?

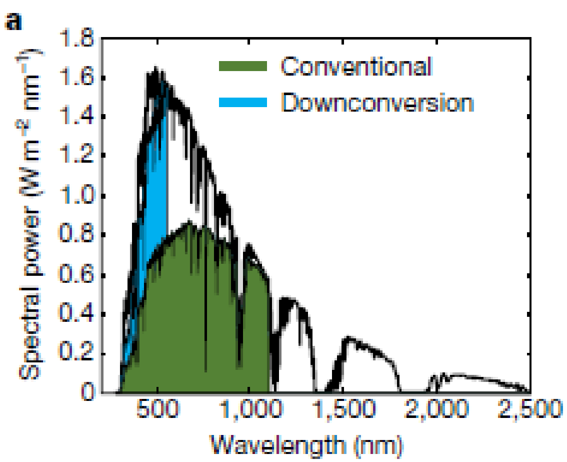


organic

Si

SF donor: tetracene
Acceptor: n-Si



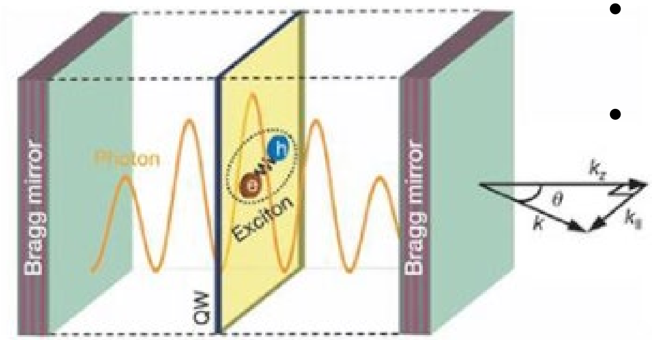


#exciton transferred to Si/#exciton in Tc = 1.33

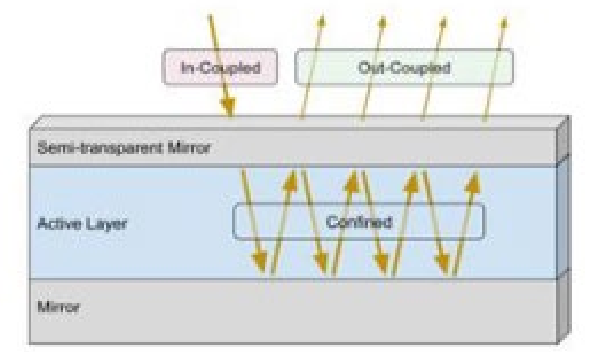
- Organic layer helps harvest photons which Si is unable to utilize !
- Design better materials and interfaces

Einzinger et al., Sensitization of silicon by singlet fission in tetracene, *Nature* **571**, 90 (2019)

Combining photonics and electronics



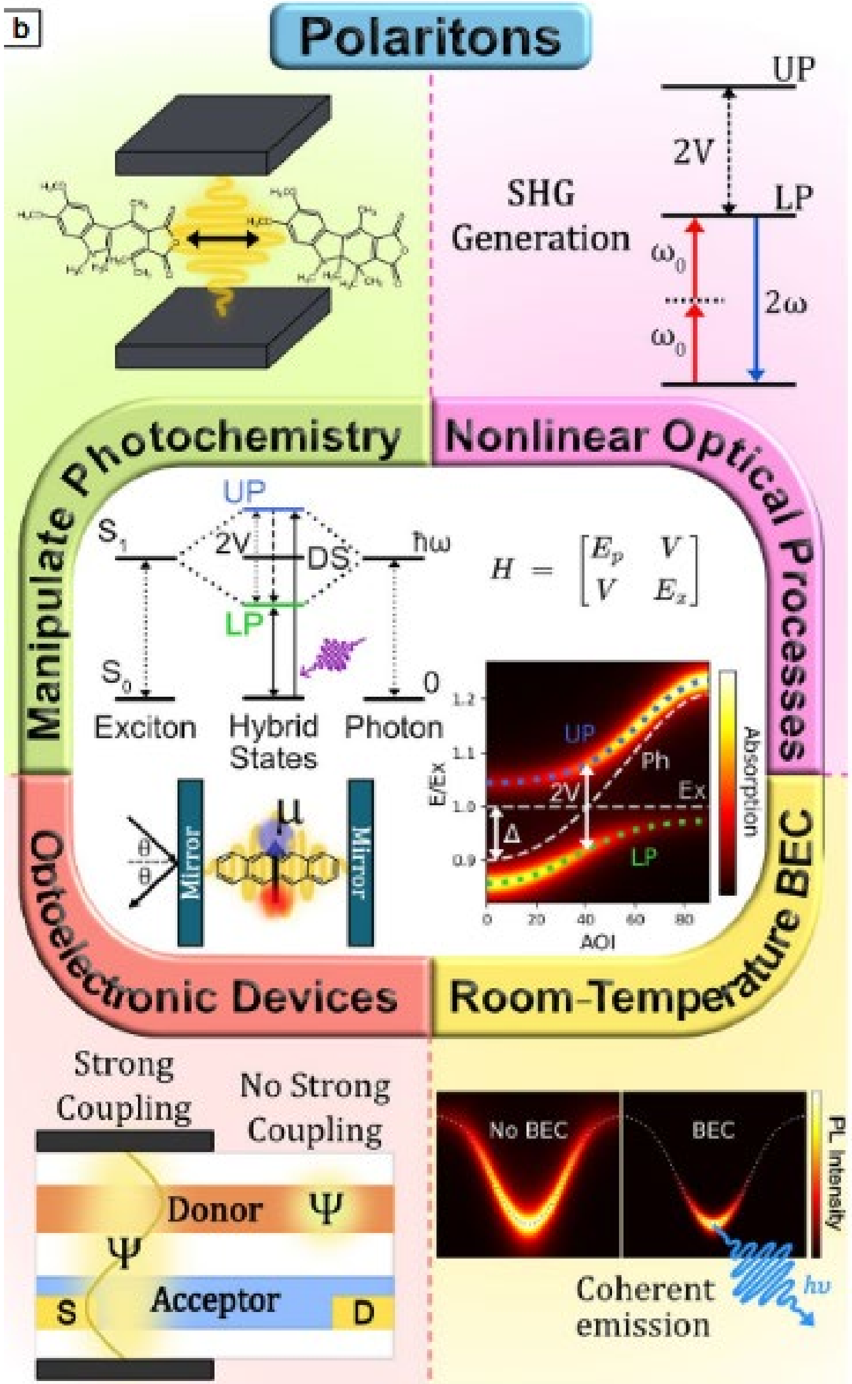
Kasprzak et al., Nature **443**, 7110 (2006)

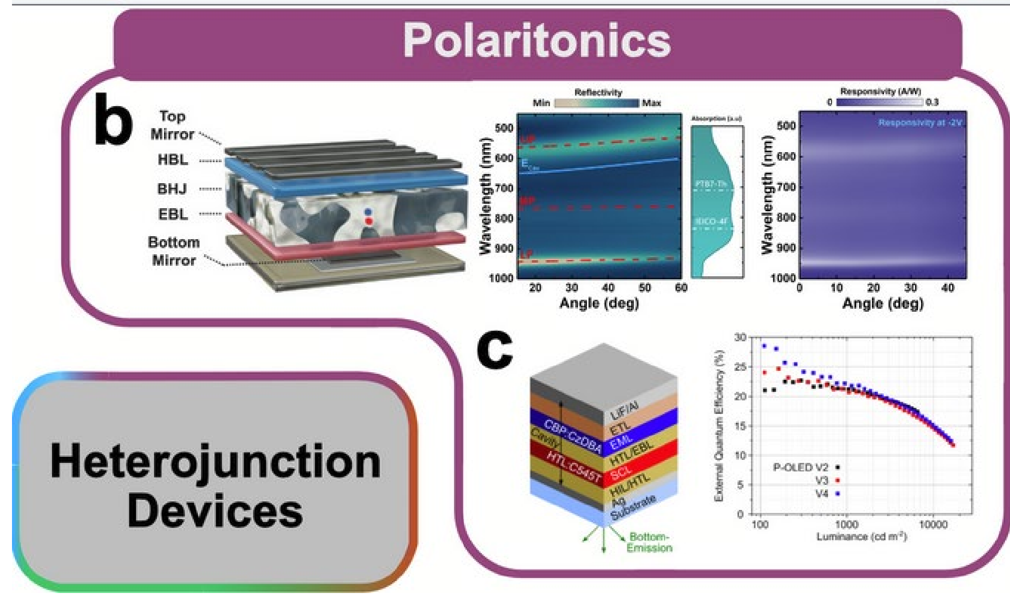


- Place organic film in a microcavity (between two mirrors)
- Electron-hole pair (exciton) + photon trapped in a cavity = light-matter hybrid particle (polariton)

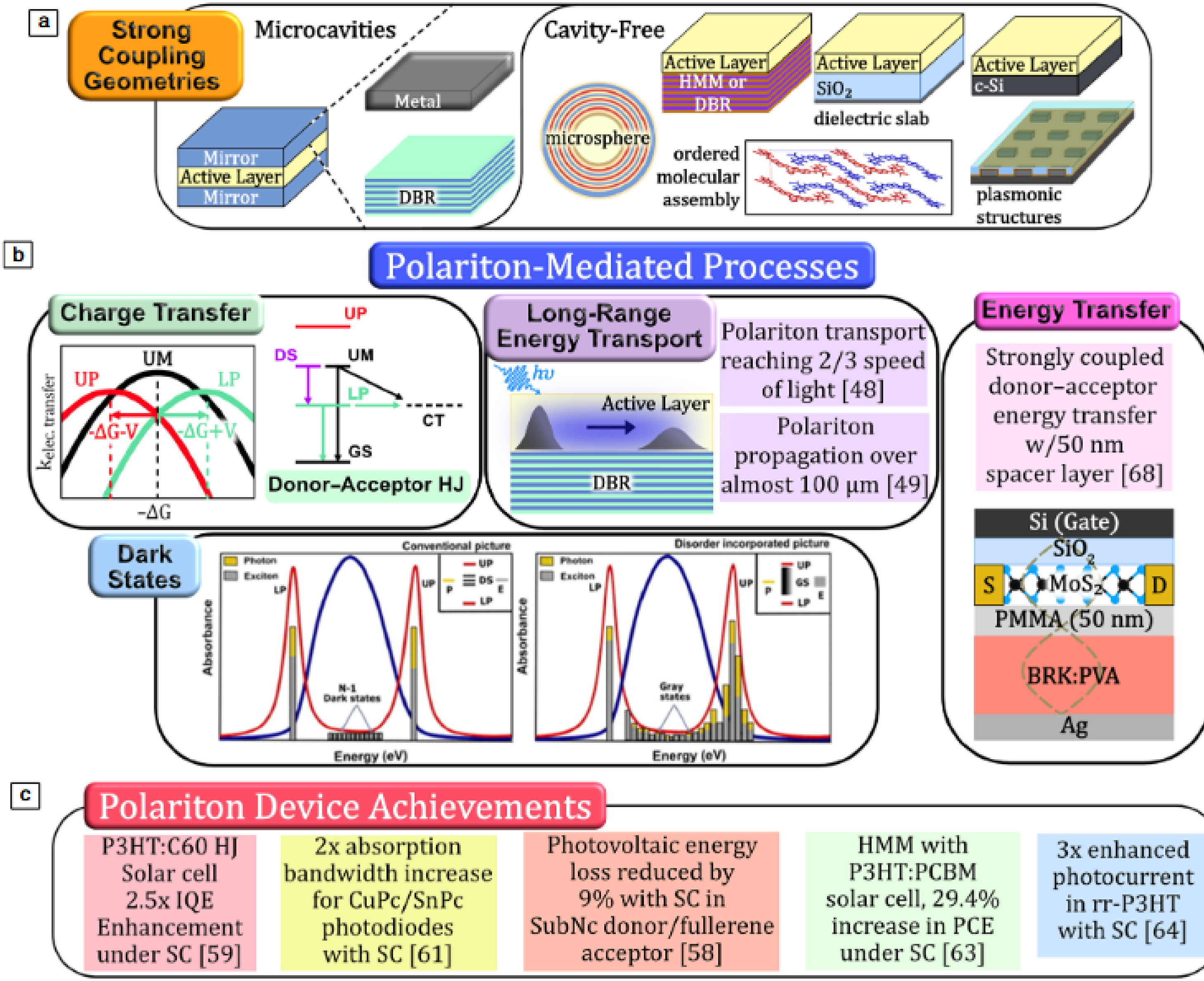
Polariton formation modifies optical and electronic properties !

Control polariton properties by cavity structure (reflectance of mirrors and film thickness)





- Polariton-enhanced OLEDs and photodetectors
- Energy transfer on micron scales
- Manipulate charge transfer with cavity detuning
- …..



a
Strong Coupling Geometries
Microcavities
Metal
Mirror
Active Layer
Mirror
DBR
Cavity-Free
Active Layer
HMM or DBR
Active Layer
SiO_2
dielectric slab
Active Layer
c-Si
microsphere
ordered molecular assembly
plasmonic structures
b
Polariton-Mediated Processes
Charge Transfer
UM
UP
LP
-ΔG-V
-ΔG+V
$k_{elec.\ transfer}$
-ΔG
UP
DS
UM
LP
CT
GS
Donor-Acceptor HJ
Long-Range Energy Transport
hν
Active Layer
DBR
Polariton transport reaching 2/3 speed of light [48]
Polariton propagation over almost 100 μm [49]
Energy Transfer
Strongly coupled donor–acceptor energy transfer w/50 nm spacer layer [68]
Si (Gate)
SiO_2
S
MoS_2
D
PMMA (50 nm)
BRK:PVA
Ag
Dark States
Conventional picture
Disorder incorporated picture
Photon
Exciton
LP
UP
N-1 Dark states
Gray states
Absorbance
Energy (eV)
c
Polariton Device Achievements
P3HT:C60 HJ Solar cell 2.5x IQE Enhancement under SC [59]
2x absorption bandwidth increase for CuPc/SnPc photodiodes with SC [61]
Photovoltaic energy loss reduced by 9% with SC in SubNc donor/fullerene acceptor [58]
HMM with P3HT:PCBM solar cell, 29.4% increase in PCE under SC [63]
3x enhanced photocurrent in rr-P3HT with SC [64]

Molecular Electronics.

- Possibility proved by both theoretical and experimental work.

1). In 1974, Aviram and Ratner proposed the idea of molecular diode for rectifying, followed by many other theoretical researches.

A. Aviram, & M.A. Ratner Chem. Phys. Lett. ***29****, 277 (1974).*

"Molecular Rectifiers"

“Molecular rectifiers”

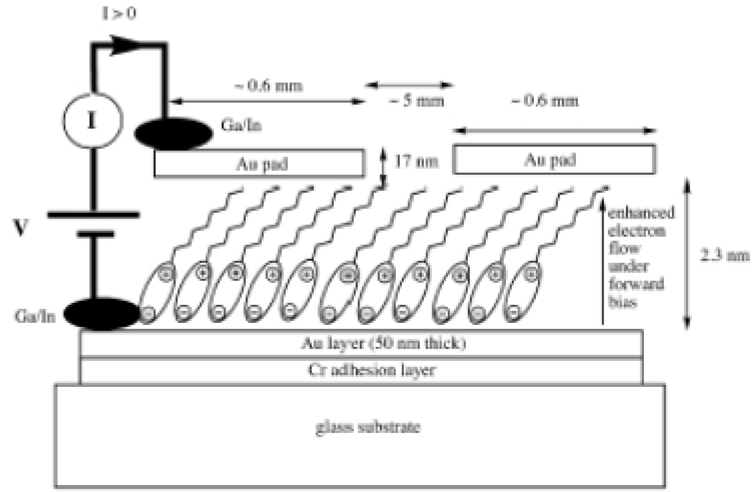
Arieh Aviram and Mark A. Ratner

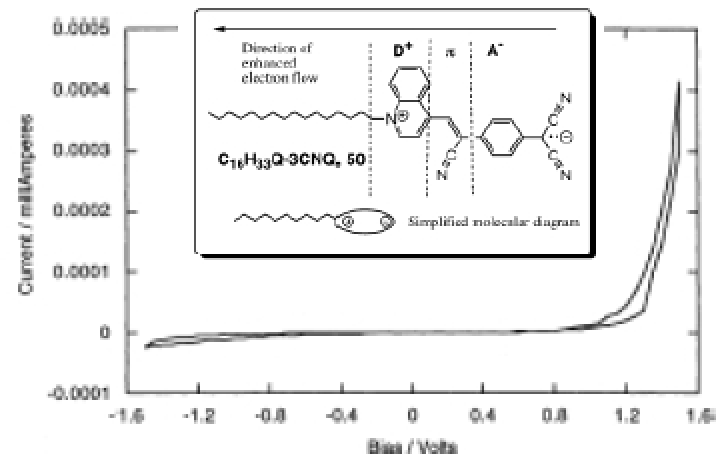
(Chem. Phys. Lett., 1974)

“The construction of a very simple electronic device, a rectifier, based on the used of a single organic molecule is discussed. The molecular rectifier consists of a donor pi system and a acceptor pi system, separated by a sigma-bonded (methylene) tunneling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.”

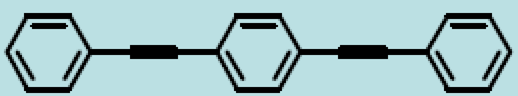
(... 23 years later)

R. Metzger et al., JACS 1997





Highly Conductive Molecular Wires

	Cross-section size (nm^2)	Current Density (electrons/nm^2 sec)
1 mm copper wire	~ 3×10^{12}	~ 2×10^{6}
	~ 0.05	~ 4×10^{12}
Carbon nanotube	~ 3	~ 2×10^{11}

The Reality of Molecular Electronics

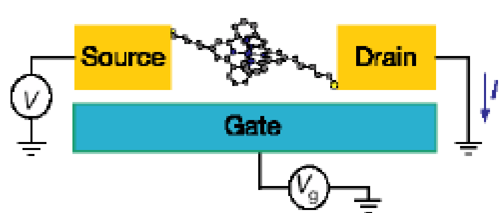
Ultimate goal --- Interconnecting and integrating million or billions of molecular units into a functional *chip*.

Challenge ---

An Intel Core 2 Duo chip has ~290 M transistors; if replaced by molecular units, need billions of molecules

Long Term Approach --- large scale assembly and organization of molecules.

Short Term Promise --- *Single-Molecule Devices (switch & sensor).*
Understanding of the fundamental processes of charge transfer through molecules and interfaces.



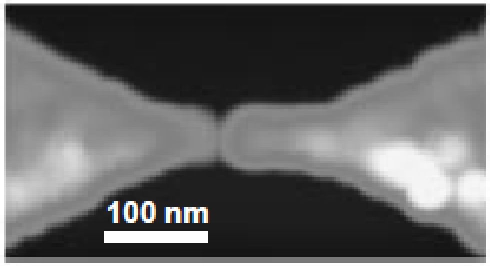
<u>Challenges of *Current/Voltage* (I/V) Measurement</u>

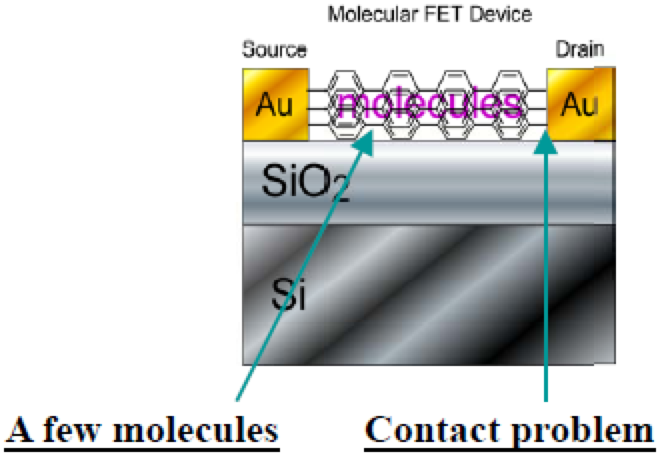
- Contact Problem --- *molecules really bonded to the electrode?*

- Single-Molecule? --- *not sure.*

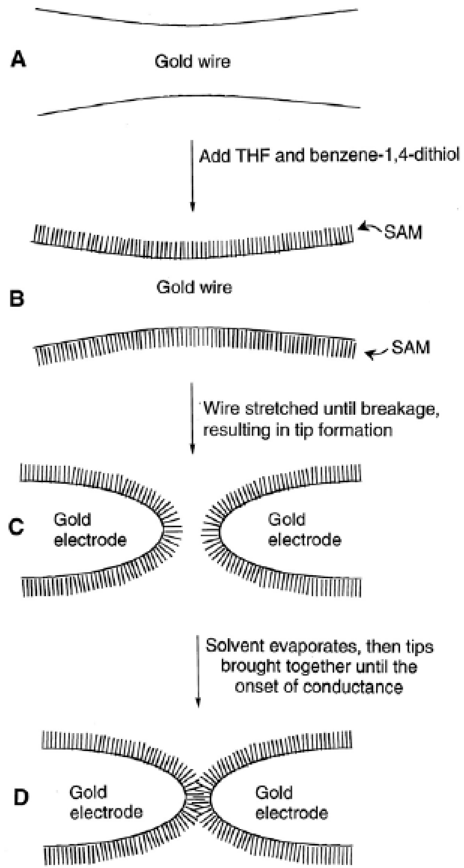
- Measurement --- *ensemble and average.*

- Electrode Fabrication --- *low production yield for small gap.*





The first break-junction by Reed



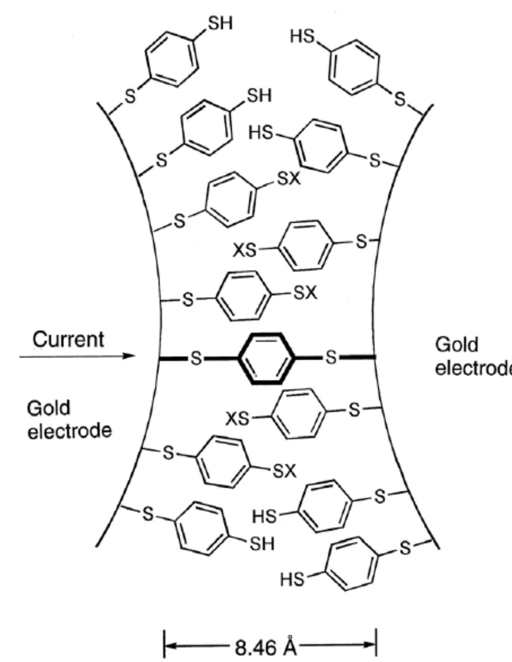
(**A**) The gold wire of the break junction before breaking and tip formation.

(**B**) After addition of benzene-1,4-dithiol, SAMs form on the gold wire surfaces.

(**C**) Mechanical breakage of the wire in solution produces two opposing gold contacts that are SAM-covered.

(**D**) After the solvent is evaporated, the gold contacts are slowly moved together until the onset of conductance is achieved.

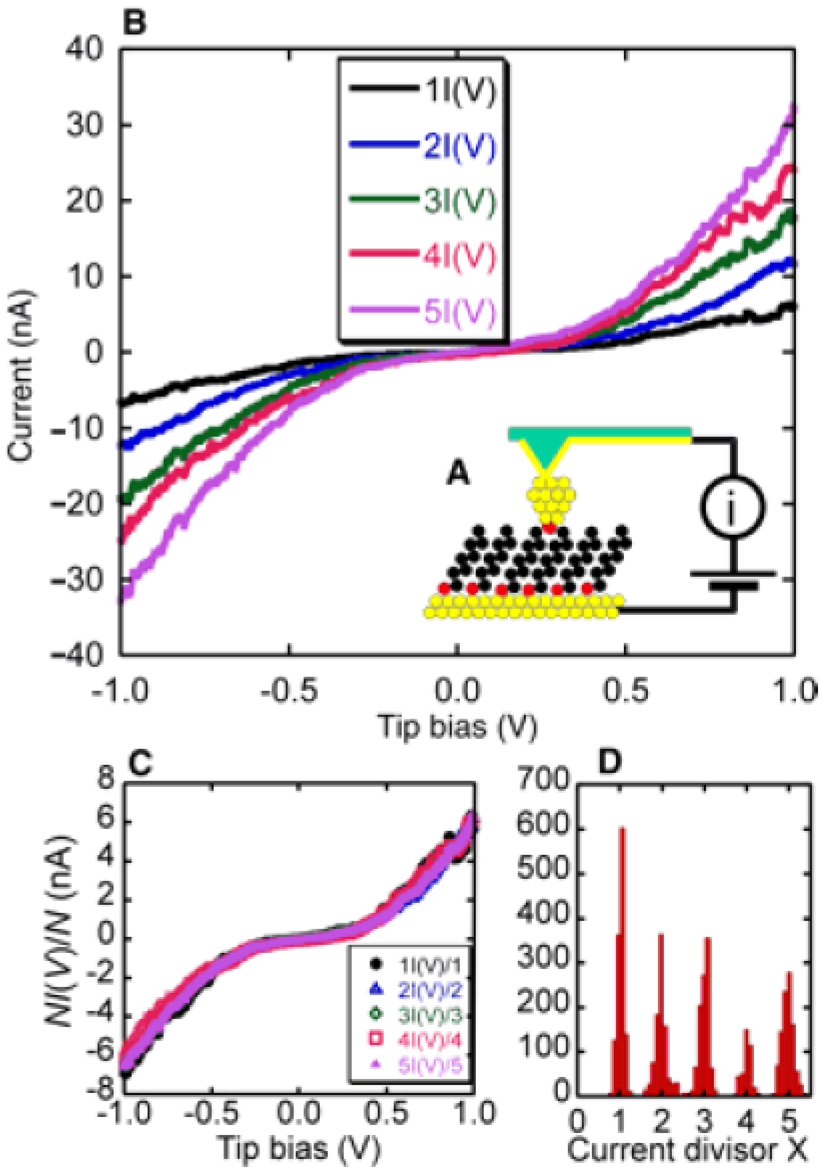
Reed and Tour; SCIENCE, VOL. 278, 1997, p252



Significance

- Wiring a single molecule into an electrical circuit by chemically bonding each end to a metal conductor is a key requirement for molecule-based electronics.
- Although conceptually simple, this goal has proven elusive.
- A wide variety of methods have been developed and used for contacting molecules.
- However, unambiguous contact to a **single molecule** is difficult to achieve, as shown by large disparities in conductivities reported for identical or similar molecules.
- Calculated conductivity can disagree with experimental results by several orders of magnitude.
- In many cases, electrical connections to the molecules have been made via **nonbonded** mechanical contacts rather than chemical bonds, and it is likely that this may account for some of the discrepancies.

Science,2001,294,571



(**A**) Schematic representation of the experiment. The sulfur atoms (red dots) of octanethiols bind to a sheet of gold atoms (yellow dots), and the octyl chains (black dots) form a monolayer. The second sulfur atom of a 1,8-octanedithiol molecule inserted into the monolayer binds to a gold nanoparticle, which in turn is contacted by the gold tip of the conducting AFM.

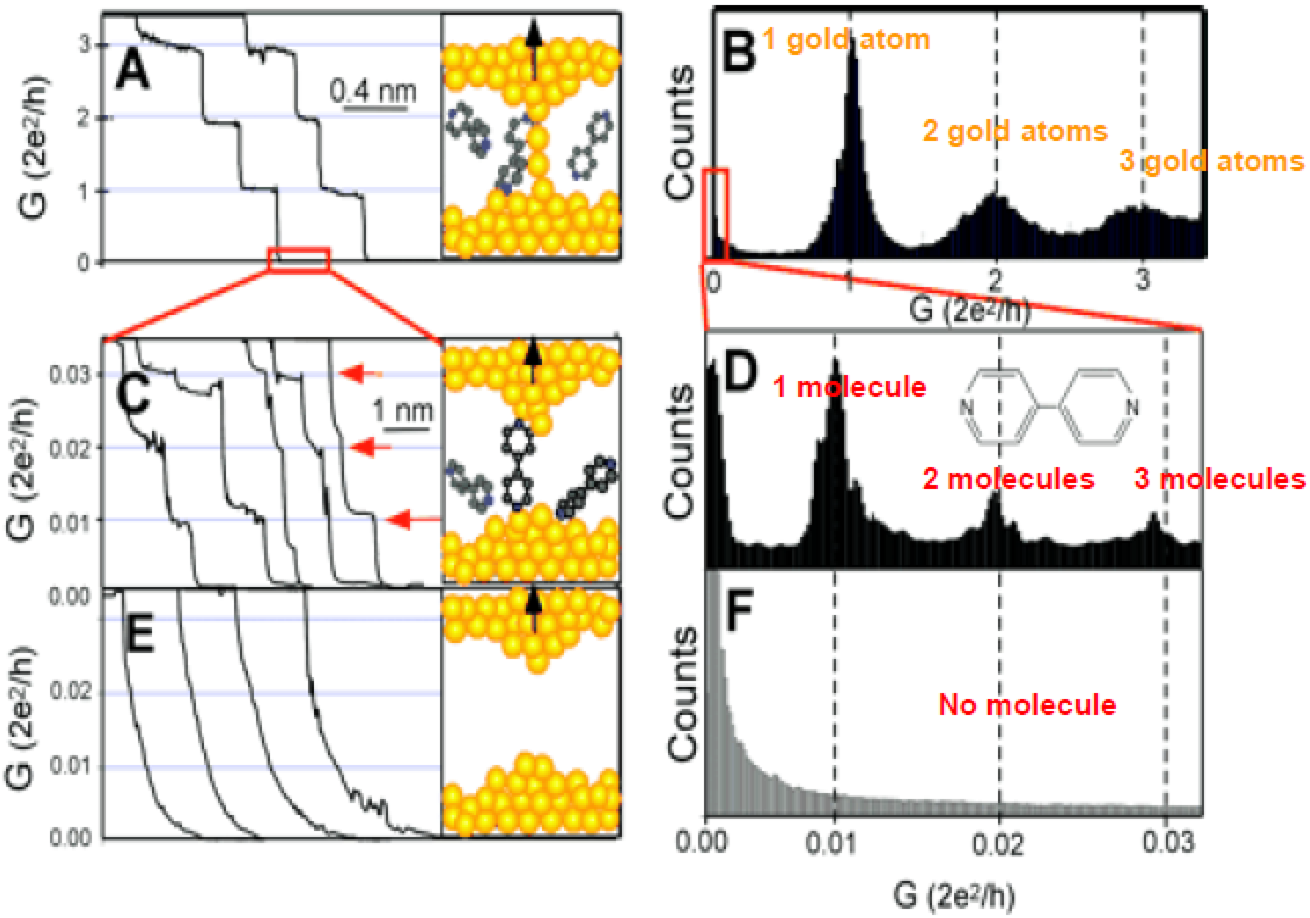
(**B**) *I*(*V*) curves measured with the apparatus diagrammed in (A). The five curves shown are representative of distinct families, *NI*(*V*), that are integer multiples of a fundamental curve, *I*(*V*) (*N* = 1, 2, 3, 4, and 5).

(**C**) Curves from (B) divided by 1, 2, 3, 4, and 5.

(**D**) Histogram of values of a divisor, *X* (a continuous parameter), chosen to minimize the variance between any one curve and the fundamental curve, *I*(*V*). It is sharply peaked at integer values 1.00 ± 0.07 (1256 curves), 2.00 ± 0.14 (932 curves), 3.00 ± 0.10 (1002 curves), 4.00 ± 0.10 (396 curves) and 5.00 ± 0.13 (993 curves). (Spreads are ±1 SD.) Of 4579 randomly chosen curves, over 25% correspond to the *X* = 1 (single-molecule) peak.

Setup: conducting AFM.

Science,2001,294,571

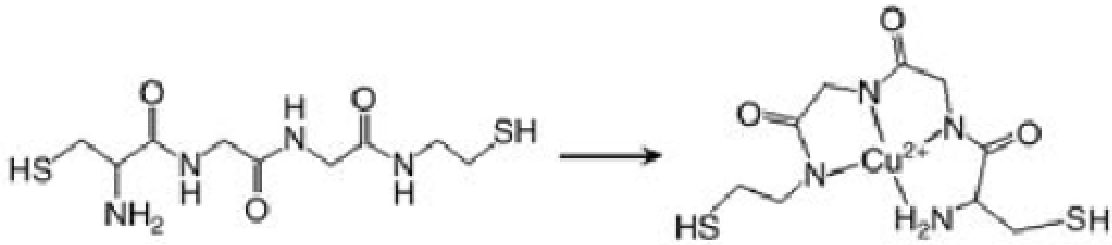


(**A**) Conductance of a gold contact formed between a gold STM tip and a gold substrate decreases in quantum steps near multiples of G_0 (= $2e^2/h$) as the tip is pulled away from the substrate. (**B**) A corresponding conductance histogram constructed from 1000 conductance curves as shown in (A) shows well-defined peaks near 1 G_0, 2 G_0, and 3 G_0 due to conductance quantization. (**C**) When the contact shown in (A) is completely broken, corresponding to the collapse of the last quantum step, a new series of conductance steps appears if molecules such as 4,4' bipyridine are present in the solution. These steps are due to the formation of the stable molecular junction between the tip and the substrate electrodes. (**D**) A conductance histogram obtained from 1000 measurements as shown in (C) shows peaks near 1 x, 2 x, and 3 x 0.01 G_0 that are ascribed to one, two, and three molecules, respectively. (**E** and **F**) In the absence of molecules, no such steps or peaks are observed within the same conductance range.

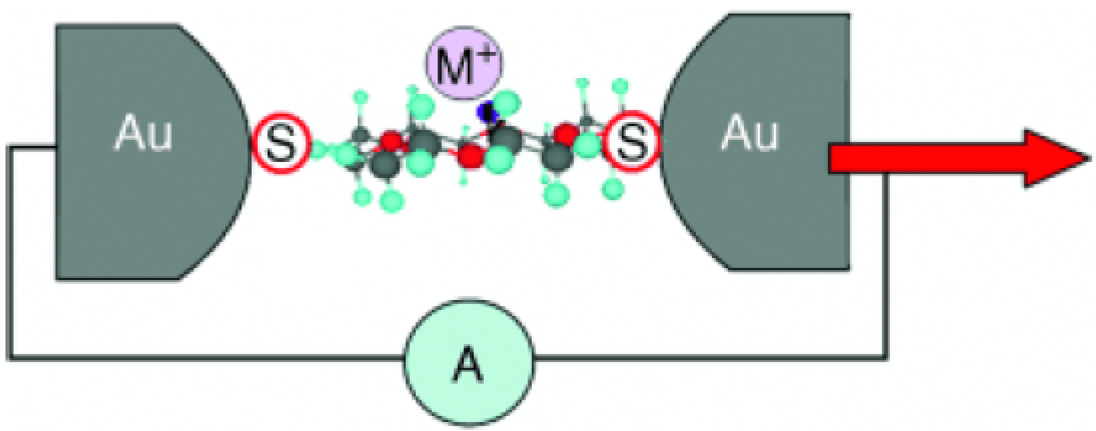
All STM techniques!

Science,2003,301,1221

Single-molecule sensor for metal ions

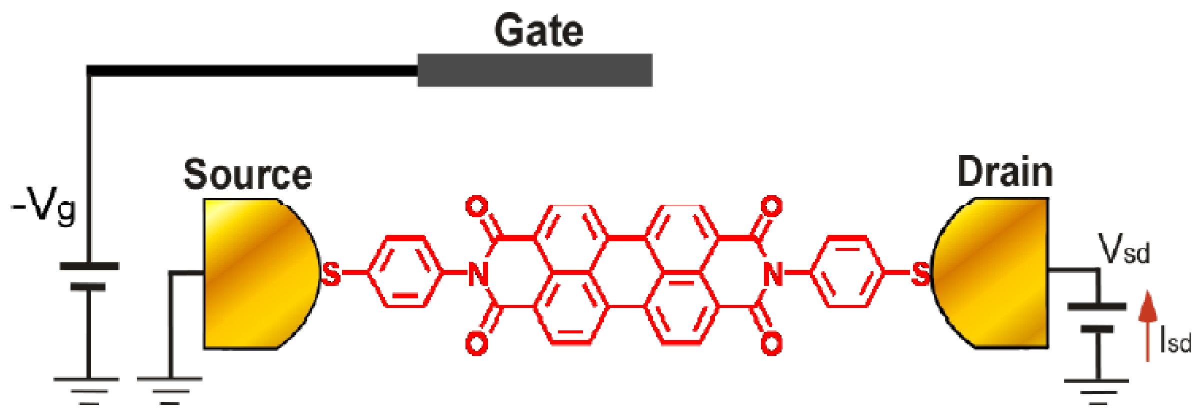


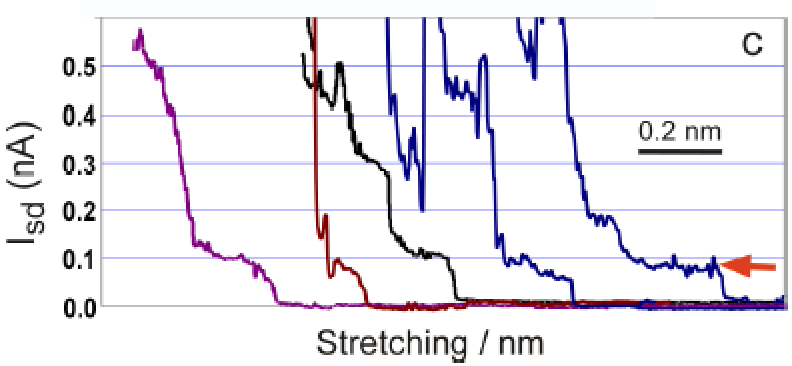
Conductivity increased upon metal binding!

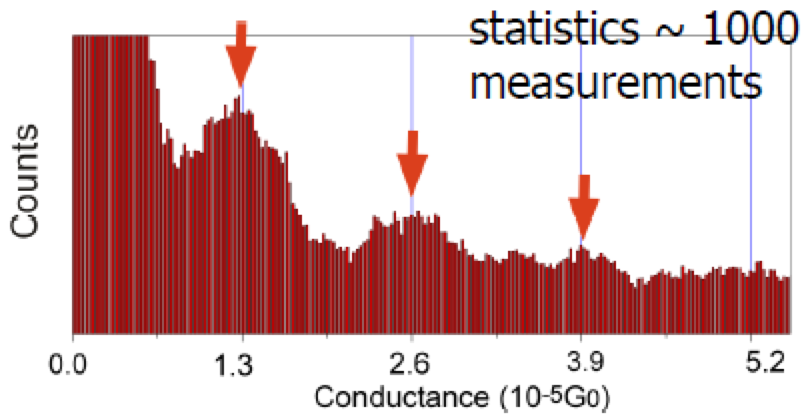


Angewchem, 2004,43,6148

Single-molecule FET



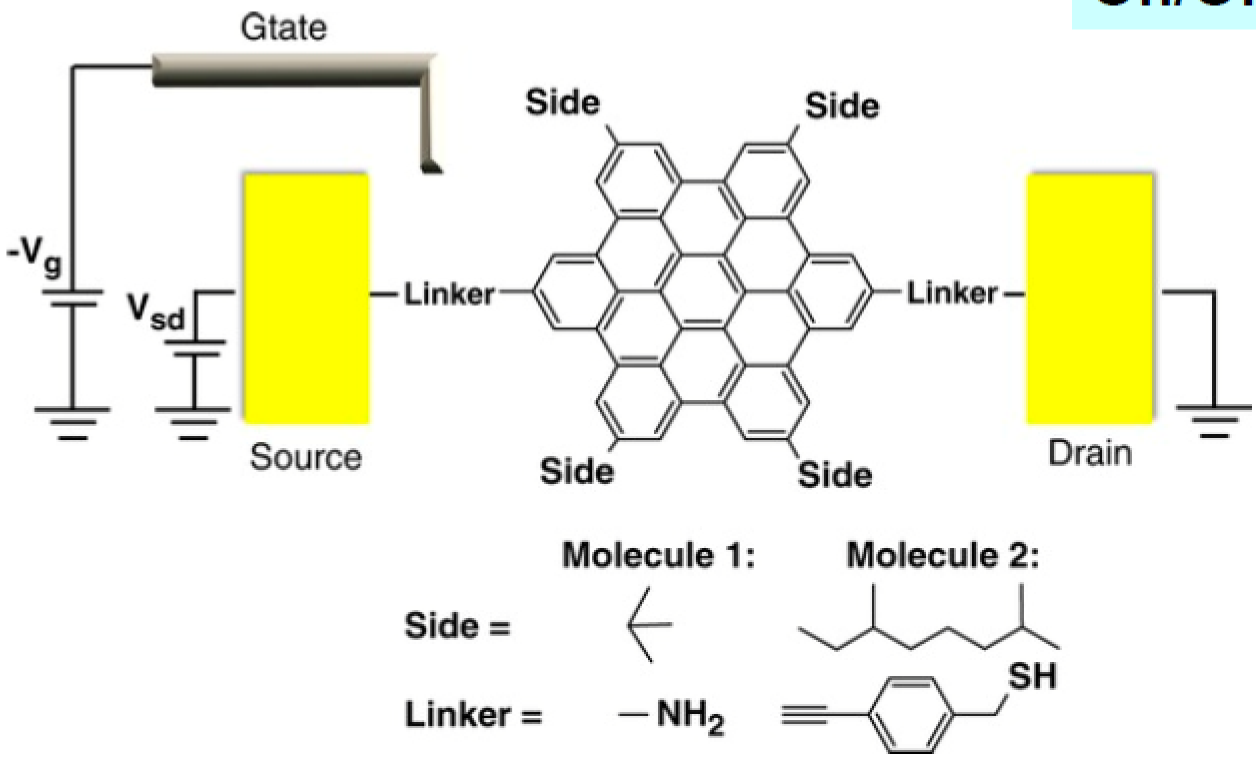




Zang and Tao et al. ***J. Am. Chem. Soc.* 127** (2005) 2386-2387 .

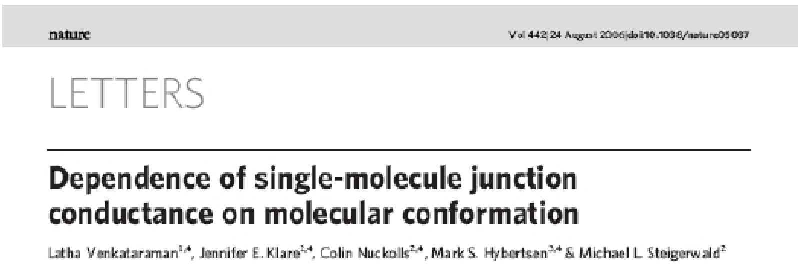
bottom-up approach towards graphene transistors

On/Off ratio ~ 10^2



Zang, Tao et al. Nature Commun. **1**, (2010) doi:10.1038/ncomms1029.

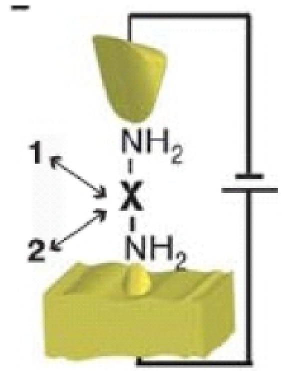
1.3 Role of the conjugation in molecular wires


nature Vol 442|24 August 2006|doi:10.1038/nature05037

LETTERS

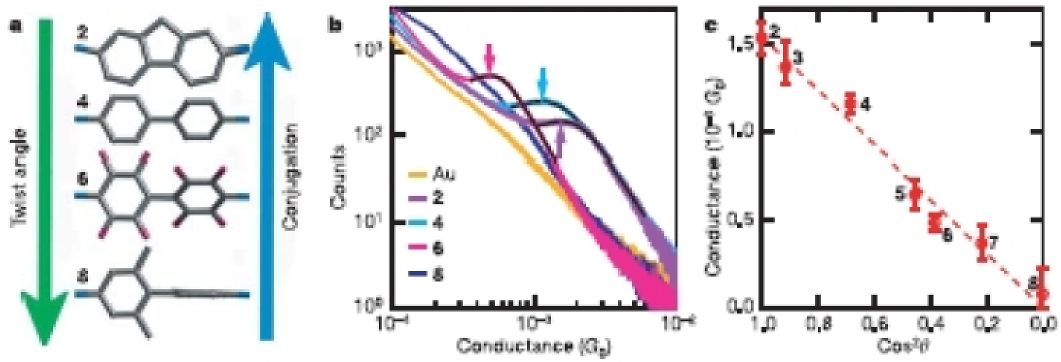
Dependence of single-molecule junction conductance on molecular conformation

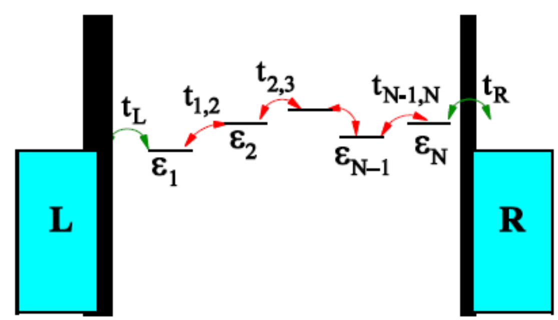
Latha Venkataraman[1,4], Jennifer E. Klare[2,4], Colin Nuckolls[2,4], Mark S. Hybertsen[3,4] & Michael L. Steigerwald[2]



$$G = \frac{2e^2}{h} T(E_F)$$

Influence of the conjugation (two-ring molecules)



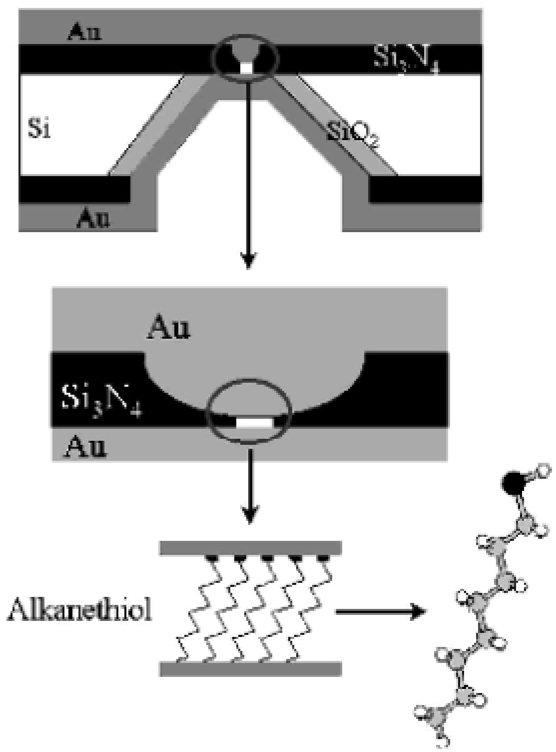


In a conjugated molecule, the coupling between different segments is mediated by a $\pi-\pi$ hopping element

$$t_{\pi-\pi} = t_0 \cos\theta \Rightarrow T \propto \cos^2\theta$$

Length dependence of conductance

Wang, Lee and Reed, PRB 68, 035416 (2003)



The conductance decays exponentially with the length of the molecule

$$G = G_0 e^{-\beta d}$$

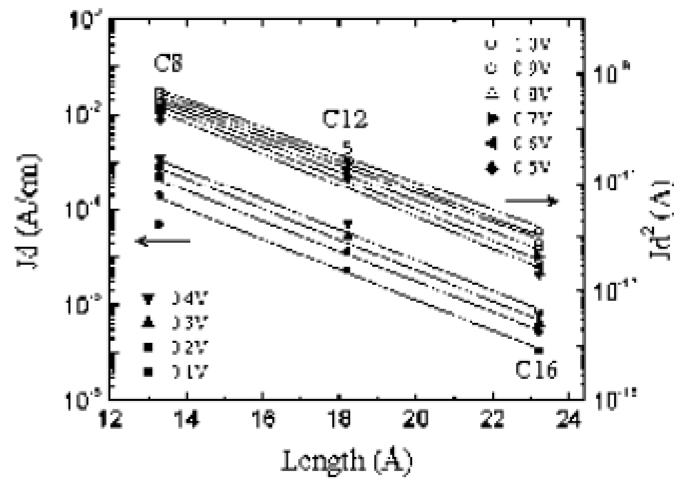


FIG. 6. Log plot of tunneling current densities multiplied by molecular length d at low bias and by d^2 at high bias (symbols) vs molecular lengths. The lines through the data points are linear fittings.

Marcus expressions for non-adiabatic ET rates

$$k_{D\to A} = \frac{2\pi}{\hbar} |V_{DA}|^2 \, \mathrm{F}(E_{AD})$$

$$= \frac{2\pi}{\hbar} \left|V_{D1}V_{NA}\right|^2 \left|G_{1N}^{(B)}(E_D)\right|^2 \mathrm{F}(E_{AD})$$

Donor-to-Bridge/ Acceptor-to-bridge

Bridge Green's Function

$$\mathrm{F}(E) = \frac{e^{-(\lambda+E)^2/4\lambda k_B T}}{\sqrt{4\pi\lambda k_B T}}$$

Franck-Condon-weighted DOS

Reorganization energy

Bridge mediated ET rate

$$k_{ET} \sim \mathrm{F}\,(E_{AD},T)\exp(-\beta' R_{DA})$$

β' (Å^{-1})=

0.2-0.6 for highly conjugated chains

0.9-1.2 for saturated hydrocarbons

~ 2 for vacuum

A relation between g and k

Electron charge

$$g \approx \frac{8e^2}{\pi^2 \Gamma_D^{(L)} \Gamma_A^{(R)} F} k_{D \to A}$$

conduction

Decay into electrodes

Marcus

Electron transfer rate

A relation between g and k

$$g \approx \frac{8e^2}{\pi^2 \Gamma_D^{(L)} \Gamma_A^{(R)} \mathsf{F}} k_{D\to A}$$

$$\mathsf{F} = \left(\sqrt{4\pi\lambda k_B T}\right)^{-1} \exp\left(-\lambda / 4k_B T\right)$$

$\lambda \approx 0.5\text{eV}$ $\quad\quad$ $\Gamma_D^{(L)} = \Gamma_A^{(R)} \approx 0.5eV$

$$g \sim \left(e^2/\pi\hbar\right)\left(10^{-13} k_{D\to A}(s^{-1})\right)$$
$$\cong \left[10^{-17} k_{D\to A}(s^{-1})\right]\Omega^{-1}$$