FERROELECTRICITY: FROM ORGANIC CONDUCTORS TO CONDUCTING POLYMERS

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- Conducting polymers 1978-2008.
  electrical conduction and optical activity.
- Modern requests for ferroelectric applications and materials.
- Existing structural ferroelectricity in a saturated polymer.
- Ferroelectric Mott-Hubbard phase and charge disproportionation in quasi 1d organic conductors.
- *Expectations of the electronic ferroelectricity in conjugated modified polyenes.*

Ferroelectricity is a rising demand in fundamental and applied solid state physics.

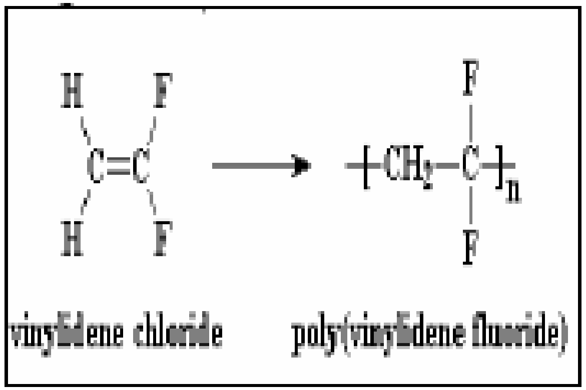
- Active gate materials and electric RAM in microelectronics,
- Capacitors in portable WiFi communicators,
- Electro-Optical-Acoustic modulators,
- Electro-Mechanical actuators
- Transducers and Sensors in medical imaging.

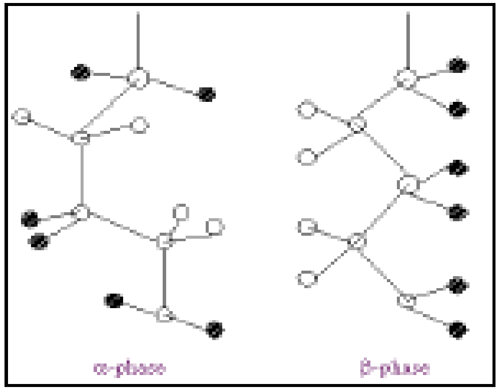
Request for plasticity – polymer-ceramic composites

but weakening responses – effective $\varepsilon \sim 10$.

Plastic ferrroelectrics are necessary in medical imaging – low weight : compatibility of acoustic impedances with biological tissues.

Ferroelectrics are available mostly in the inorganic world.
Can we have organic only, particularly polymer only ferroelectric ?





PVDF substitutes polyethylene – saturated polymer

➢**One ferroelectric saturated polymer does exist - Poly(vinylidene flouride) PVDF :**

- **ferroelectric and pyroelectric,**
- **efficient piezoelectric if poled – quenched under a high voltage.**

➢ **Light, flexible, non-toxic, cheap to produce**

➢ **Helps in very costly applications:**

- **ultrasonic transducers**
- **hydrophone probes, sonar equipment**
- **unique as long stretching actuator.**

but: ε~10 – modest efficiency (compare to ε~500 – 15000 for inorganic FE)

Can we go wider, diversely, and may be better with *conjugated polymers*?
Can we mobilize their fast pi-electrons to make a better job than common ions?

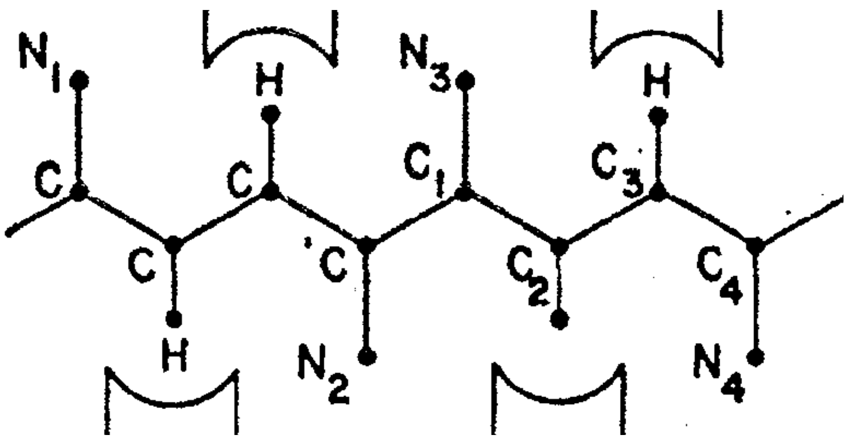
PHYSICAL REVIEW VOLUME 134, NUMBER 6A 15 JUNE 1964

Possibility of Synthesizing an Organic Superconductor*

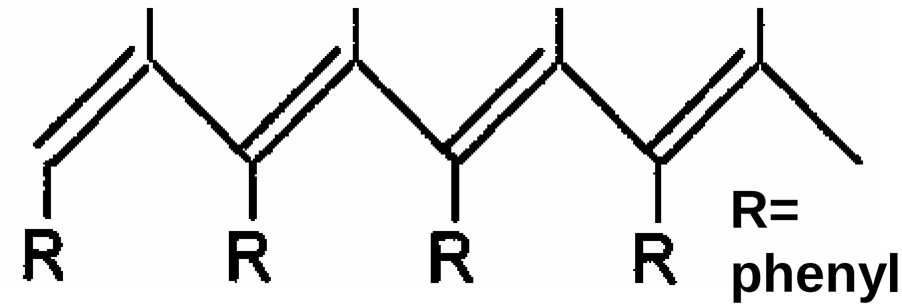
W. A. Little
Department of Physics, Stanford University, Stanford, California
(Received 13 November 1963; revised manuscript received 27 January 1964)

« In the beginning was the Word, …
and without him was not anything made that was made »

But was "organic supercondictivity" the only promised land?
Not quite : some of the profet's visions actually imply a spontaneous electric polarization, hence they are FERROELECTRIC.



Drawing from the PRB 1964
It is a pyroelectric if N≠H



Later popular drawing (Sci. Am.)
It must be a ferroelectric if R≠H
also an illustration of conjugated polymer

Conducting polymers: today's applications

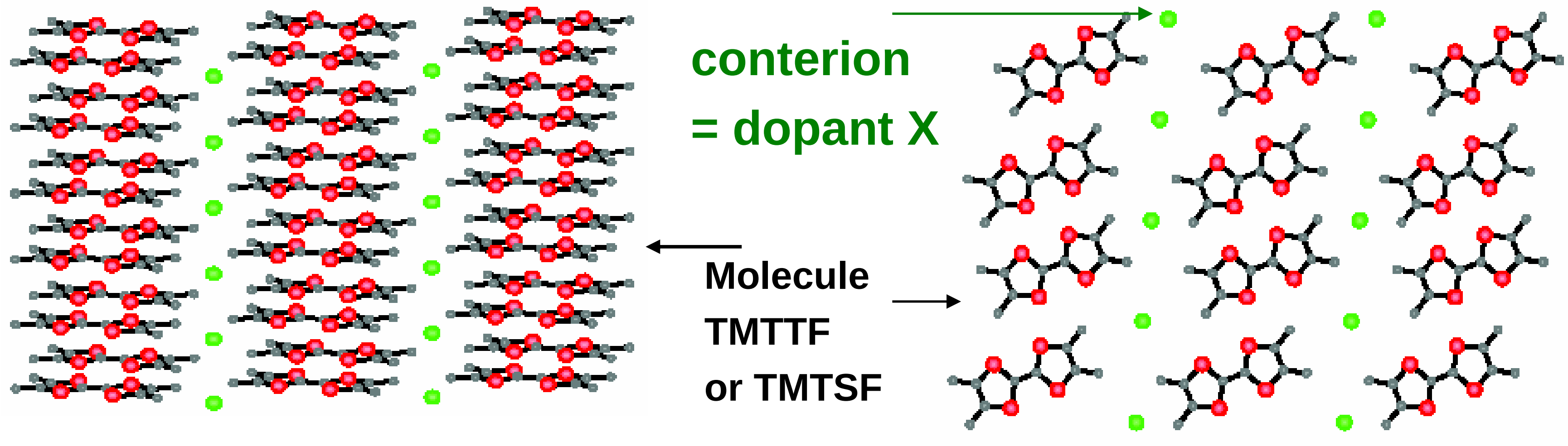
LED display and microelectronic chip made by Phillips Research Lab

Tsukuba, LED TV.

Ferroelectricity in conjugated polymers?

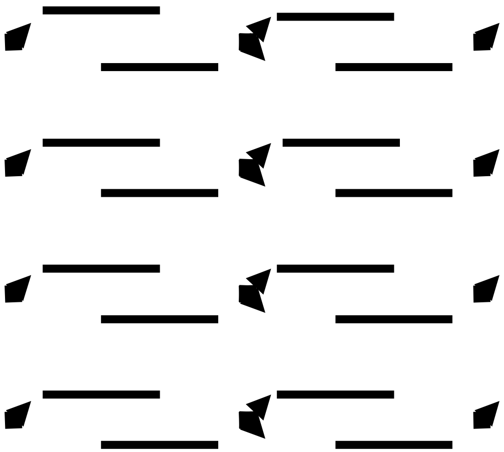
- Where does the confidence come?
- What may be a scale of effects ?

Proved by success in organic conducting crystals.



Built-in dimerization of bonds - counterions against each second pair of molecules)

Spontaneous symmetry breaking – displacements of counterions, nonequivqlence of sites



Arrows show displacements of ions X.
They follow and stabilize the electronic charge disproportionation.

Collinear arrows – ferroelectricity.

Alternating arrows – anti-ferroelectricity.

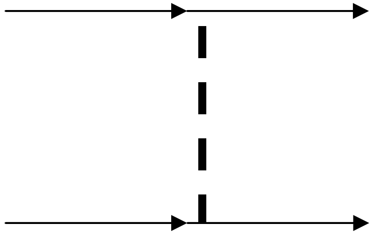
A single stack is polarized in any case.

Major polarization comes from redistribution of electronic density, hence amplification of polarizability ε by a factor of $(\omega_p/\Delta)^2 \sim 10^2$ giving even a background $\varepsilon \sim 10^3$

1D Mott-Hubburd state. 1 electron per site i.e. the half filled band.
Spin degrees of freedom are split-off and gapless.
Charge degrees of freedom can be gapful: $\Psi_{\pm} \sim \exp[\pm i\varphi / 2]$

chiral phase $\varphi=\varphi(x,t)$ for fermions near $+/-K_F$:

Gap rigin: Umklapp scattering (Luther and Emery,Dzyaloshinskii & Larkin).



Uexp[i 2φ] : amplitude of the Umklapp scattering of electrons $(-K_F, -K_F) \rightarrow (+K_F, +K_F)$ is allowed here.
Momentum deficit $4K_F$ is just compensated by the reciprocal lattice period. Contineous chiral symmetry lifting: arbitrary translations are forbidden on the lattice.

Amplitude U may have a phase α !

$$H \sim (\hbar/4\pi\gamma)\,[v_\rho\,(\partial_x\varphi)^2 + (\partial_t\varphi)^2/v_\rho] - U\cos(2\varphi-2\alpha)$$

- Hamiltonian degeneracy $\varphi \rightarrow \varphi+\pi$ originates current carriers:

  $\pm\pi$ solitons with charges $\pm e$, energy Δ

  (= holon = $4K_F$ CDW discommensuration = Wigner crystal vacancy)

COMBINED MOTT - HUBBARD STATE

2 types of dimerization ⇒

2 interfering sources for two-fold commensurability

⇒ 2 contributions to the Umklapp interaction:

Site dimerization : $H_U^s = -U_s \cos 2\varphi$ (spontaneous)

Bond dimerization : $H_U^b = -U_b \sin 2\varphi$ (build-in)

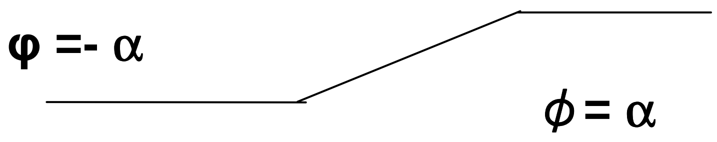
At presence of both site and bond types

$H_U = -U_s \cos 2\varphi - U_b \sin 2\varphi = -U \cos(2\varphi - 2\alpha)$

$U_s \neq 0 \rightarrow \alpha \neq 0 \rightarrow$ phase φ = "mean displacement of all electrons" shifts from $\varphi = 0$ to $\varphi = \alpha$, hence the gigantic FE polarization.

From a single stack to a crystal: Macroscopic FerroElectric ground state if the same α is chosen for all stacks,
Anti-FE state if the sign of α alternates *- both cases are observed*

Spontaneous U_s can change sign between different FE domains.
Then electronic system must also adjust its ground state from α to $-\alpha$.
Hence the domain boundary $U_s \leftrightarrow -U_s$ requires for the phase soliton of the increment $\delta = -2\alpha$
which will concentrate the *non integer* charge $q = -2\alpha/\pi$ per chain.

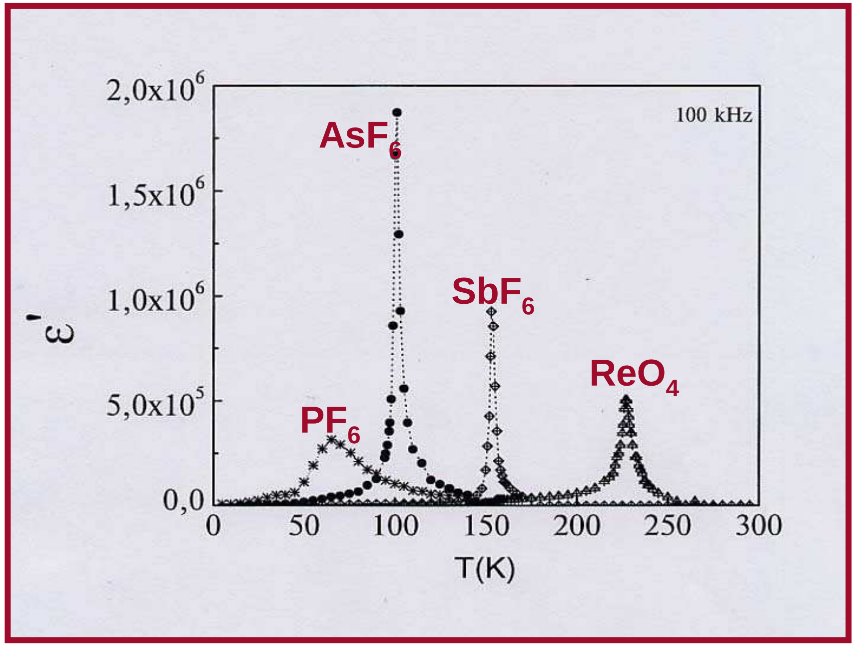


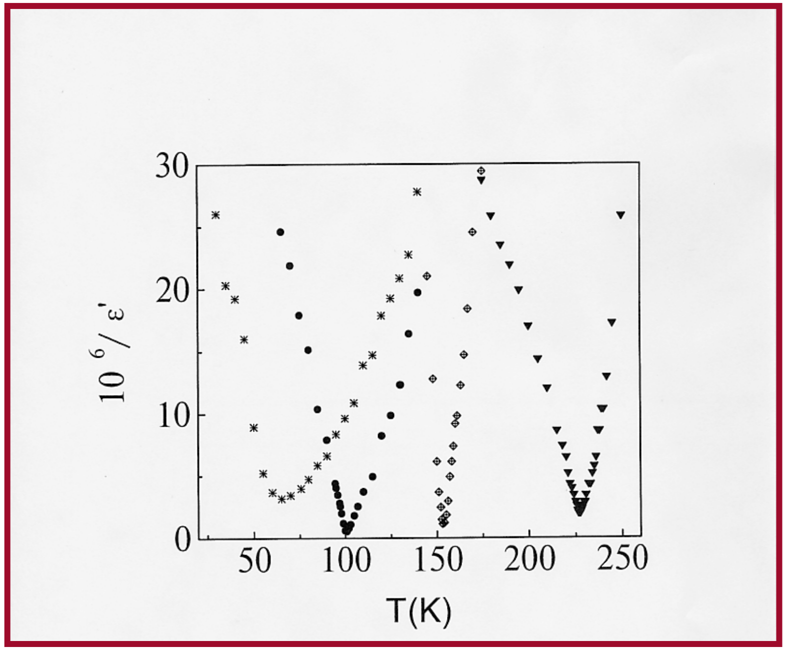
alpha- solitons are walls between domains of opposite FE polarizations

They are on-chain conducting particles only above T_{FE}.
Below T_{FE} they aggregate into macroscopic walls.
They do not conduct any more,
but determine the FE depolarization dynamics.

Real part of dielectric constant of $(TMTTF)_2X$ salts

P.Monceau F. N and S.B. Phys. Rev. Lett. 86 (2001) 4081





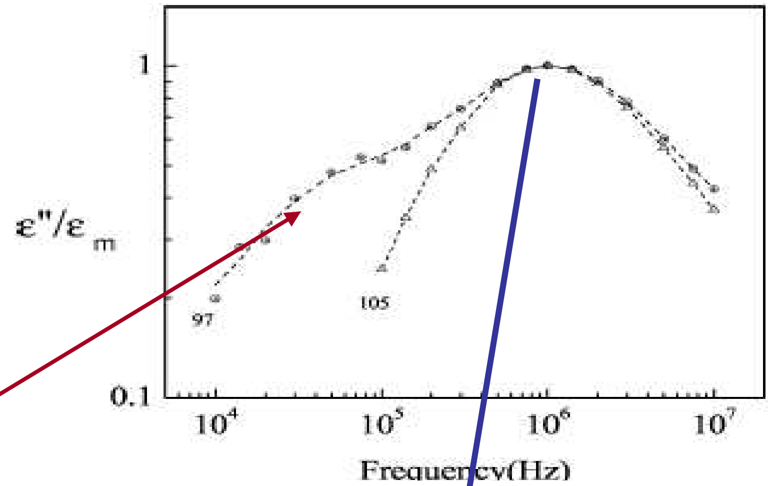
a second order phase transition described by the Curie law

$$\varepsilon' = \frac{A}{|T - T_{CO}|}$$

Dow we see the motion of FE solitons ? Yes at $T<T_c$

Frequency dependence of imaginary part of ε

Comparison of the ε´´(f) curves at two temperatures near T_c:
above - 105K and below - 97K.

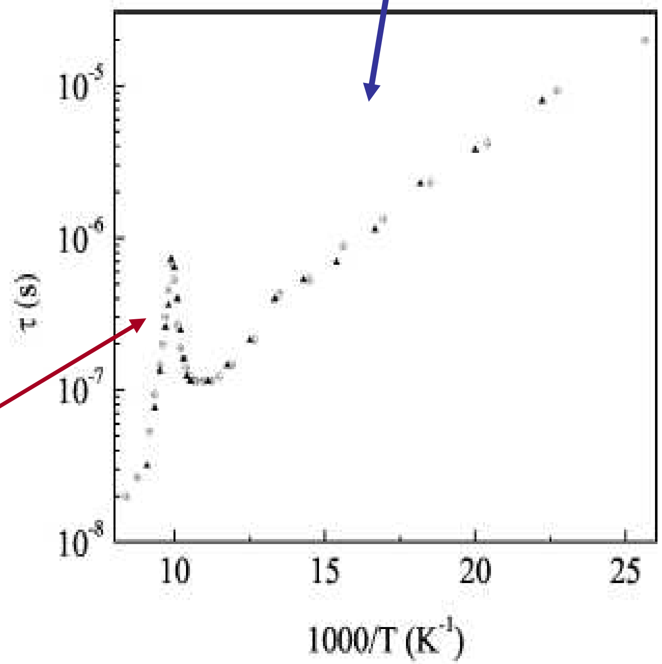


Low frequency shoulder - only at T<Tc :
pinning of FE domain walls ?

T- dependence of relaxation time for the main peak:

Critical slowing down near T_c,

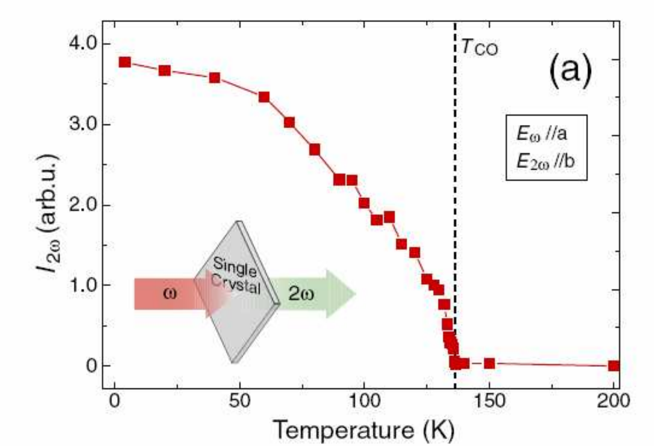
Activation law at low T – friction of FE domain walls by charge carriers



Landau-Khalatnikov critical relaxation

K. Yamamoto et al. JPSJ, 77 (2008) 074709

Second harmonic generation
λ(ω)=1400nm



Problem of identification of the frozen polarization:
through anomalous optical activity
- lack of inversion summetry

$$W = \frac{\varepsilon}{8\pi} E^2 + \chi_2 E^3$$

E^3 may exist only in case of inversion symmetry breaking

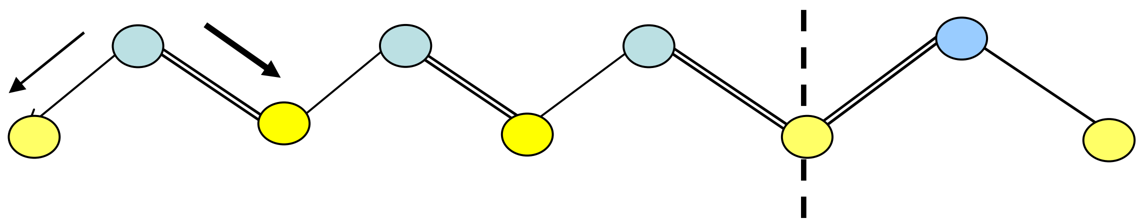
Instructions of the FE design: Combined symmetry breaking.

- ***Lift*** the inversion symmetry, remove the mirror symmetry,

  do not leave a glide plane.
- ***Keep*** the double degeneracy to get a ferroelectric.

Realization: conjugated polymers of the $(AB)_x$ type:

modified polyacetylene $(CRCR')_x$

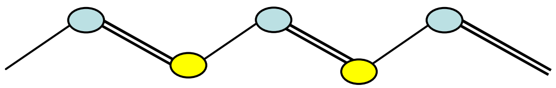


SOILITONS WITH NONINTEGER VARIABLE CHARGES:

Orthogonal mixing of static and dynamic mass generations.

Realisation: modified polyacetylene $(CRCR')_x$

Theories for solitons with variable charges: S.B. & N.K. 1981, M.Rice



$$\Delta = \sqrt{\Delta_{ex}^2 + \Delta_{in}^2}$$

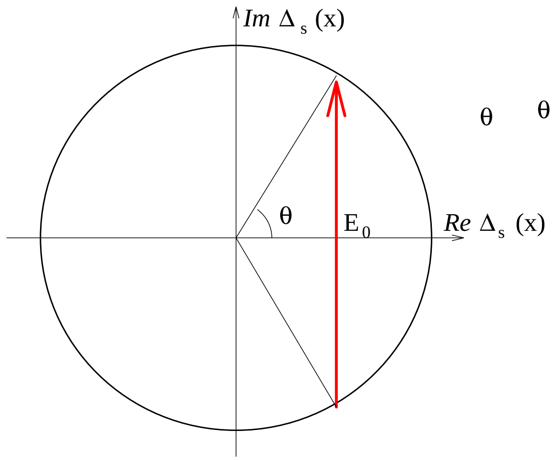
Joint effect of extrinsic Δ_{ex} and intrinsic Δ_{in} contributions to dimerization gap Δ.

Δ_{ex} comes from the build-in site dimerization – inequivalence of sites A and B.

Δ_{in} - from spontaneous dimerization of bonds $\Delta_{in}=\Delta_b$ - generic Peierls effect.

$$Tr\begin{vmatrix} -i\partial_x & \Delta_1 + i\Delta_2 \\ \Delta_1 - i\Delta_2 & i\partial_x \end{vmatrix} + K\overline{|\Delta_2|^2}$$

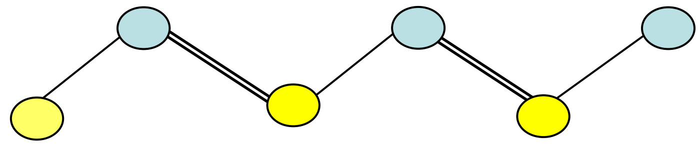
$$\Delta_1 = cnst, \quad \overline{\Delta_2} = \pm\sqrt{\Delta_0^2 - \Delta_1^2}$$



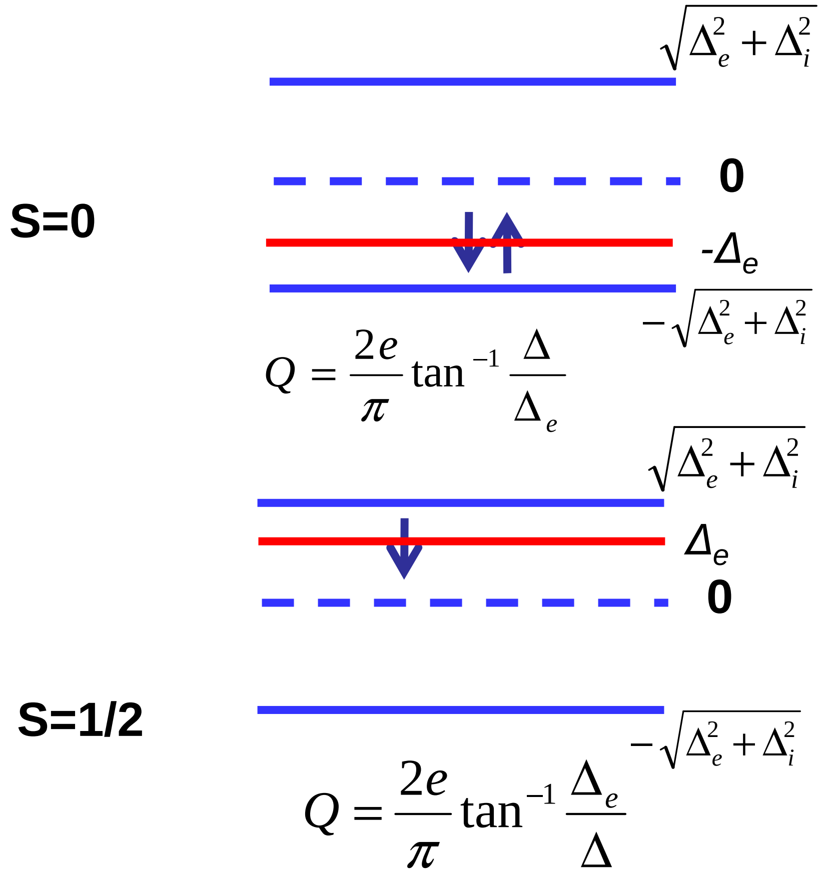
Nontrivial chiral angle $0<2\theta<\pi$ of the soliton trajectory corresponds to the noninteger electric charge $q= e\theta/\pi$

Solitonic intra-gap states

Diatomic ($C_2RR`$) chain – (AB)x polymer



Special experimental advantage:
ac electric field alternates polarization by commuting the bond ordering patterns, i.e. moving charged solitons.
Through solitons' spectral features it opens a special tool of electro-optical interference.



Δ_{in} WILL NOT be spontaneously generated – it is a threshold effect - if Δ_{ex} already exceeds the wanted optimal Peierls gap.

Chemistry precaution: make a small difference of ligands R and R'

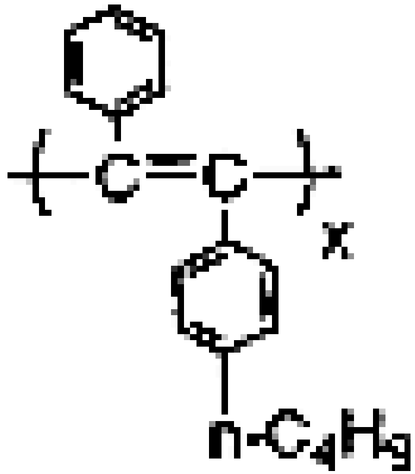
The necessary polymer does exist:

since 1999 from Kyoto-Osaka-Utah team.

By today – complete optical characterization,

indirect proof for spontaneous bonds dimerization

via spectral signatures of solitons.



“Accidental” origin of the success

to get the Peierls effect of bonds dimerization:

weak difference or radicals

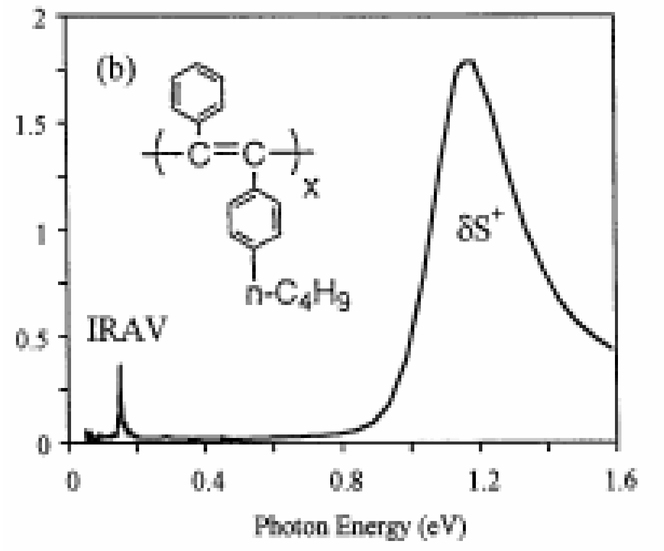
– only by a distant side group.

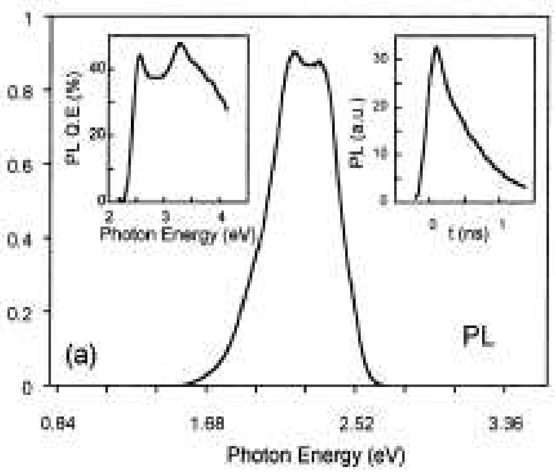
Small site dimerisation gap provoke to add the

bond dimerisation gap.

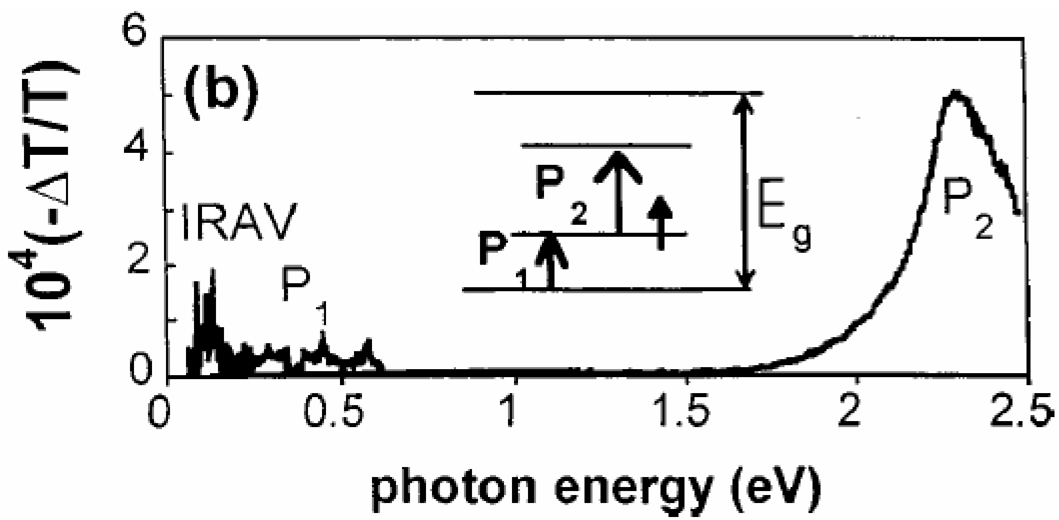
Still a missing link : no idea was to check for the Ferroelectricity:
To be tried ? and discovered !

Proof for spontaneous dimerization through the existence of solitons





Optical results by
Z.V. Vardeny group:
Soliton feature,
Absorption,
Luminescence,
Dynamics



Not a polaron, but spin soliton ?

LESSONS and PERSPECTIVES

- π-conjugated systems can support the electronic ferroelectricity.
- Effect is registered and interpreted in two families of organic crystalline conductors (quasi 1D and quasi 2D).
- Mechanism is well understood as combined collective effects of Mott (S.B. 2001) or Peierls (N.K.&S.B. 1981) types.
- An example of a must_be_ferroelectric polyene has been already studied (Vardeny et al).
- The design is symmetrically defined and can be previewed. Cases of low temperature phases should not be overlooked.
- Solitons will serve duties of re-polarization walls.

WARNINGS

1. Ferroelectric transition in organic conductors was weakly observed, but missed to be identified, for 15 years before its clarification.

2. Success was due to a synthesis of methods coming from
    a. experimental techniques for sliding Charge Density Waves,
    b. materials from organic metals,
    c. ideas from theory of conjugated polymers.

3. Theory guides only towards a single chain polarization.
   The bulk arrangement may be also anti-ferroelectric –
   still interesting while less spectacular. Empirical reason for optimism:
   majority of $(TMTTF)_2X$ cases are ferroelectrics.

4. …….

……………………..

13. High-Tc superconductivity was discovered leading by a “false idea” of looking for a vicinity of ferroelectric oxide conductors.