

A note on tunable transconductance of a branching molecular wire

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It is shown that the Griffith boundary conditions on the wavefunction of an electron moving coherently on a molecular network of one-dimensional conductors (delocalized bonds) lead to a branching resistance at the node that can be tuned resonantly. The latter provides a mechanism for regulating the transfer of an extraneous electron over a 'molecular wire' connecting two components of a supramolecular device.

It is well known that the quantum chemistry of conjugated and aromatic molecules is well described by the simple 'network model' in which the molecule is replaced by a network of straight lines (bonds) connecting neighbouring nodes (atoms), providing pathways for the motion of 'free electrons'^{1,2}. The potentials are effectively replaced by the boundary conditions on the wavefunction, namely that the latter should be single-valued and the sum of its outward derivatives should add to zero at each node³. This network model, sometimes also referred to as the free electron model, leads to resonance energy, bond order and excitation energy values to within a few per cent of those calculated by the method of molecular orbitals.

Early applications of this simple network model were concerned primarily with the energetic aspect of the problem. Recently, the emphasis has shifted to another aspect, namely, that of charge transport by these conjugated chains leading to the concept of the 'molecular wire', e.g. bispyridine polyenes⁴. For the purpose of this note we can fix our attention on the archetypal linearly conjugated trans-polyacetylene (CH)_n. Here there is a covalent backbone of σ -bonds resulting from the planar sp²-hybridization, while the π -orbitals overlap laterally to give a nominally half-filled band of delocalized π -electrons. This metallic state, of course, assumes complete resonance sans broken symmetry. The second possibility is that of dimerization that can be visualized chemically as bond alternation

(alternating single and double bonds) resulting in a broken symmetry. Physically this is the Peierls state with a gap opening at the Fermi-level (i.e. a semiconductor). Now, an extraneous electron injected into the chain can propagate as in a doped semiconductor, or more interestingly, it can lead to a charged (spinless) or neutral (spin 1/2) soliton (i.e. soliton doping). Thus, in all the three cases we can have a mobile charged object that translates along the chain and is subject to particle quantum mechanics. Hence a molecular wire.

Let us consider the transconductance of a branched molecular wire due to these charged particles. Figure 1a shows a hypothetical conjugated chain (1, 2) branched (bifurcated) at the node (3) with (3,4) as the side-chain. Figure 1b shows the equivalent network for this branched molecular wire. Let the charged particle be injected at the terminal 1 at energy $E = \hbar^2 k^2 / 2m$ with k as the wave-vector. It is partially reflected (amplitude reflection coefficient r), partially transmitted (t) with the different partial waves as shown in Figure 1b. All distances are measured away from the node (3) as the origin. Thus we have the Griffith boundary conditions³

$$\psi_1(0) = \psi_2(0) = \psi_3(0), \quad (\text{single valuedness})$$

$$\sum_i \frac{\delta \psi_i}{\delta x_i} \Big|_{\text{node}} = 0, \quad (\text{Kirchhoff law}) \quad (1)$$

with

$$\begin{aligned} \psi_1 &= \exp(-ikx_1) + r \exp(ikx_1) \\ \psi_2 &= 2s \cos k(l - x_4) \\ \psi_3 &= t \exp(ikx_2). \end{aligned} \quad (2)$$

Solving for the transmission coefficient $T \equiv |t|^2$, we get

$$T \equiv |t|^2 = 1 / (1 + \frac{1}{4} \tan^2 kl). \quad (3)$$

It is convenient to introduce transconductance as given by the Landauer formula⁵

$$G = \left(\frac{e^2}{2\pi\hbar} \right) \frac{T}{1-T} = \left(\frac{2e^2}{\pi\hbar} \right) \cot^2 kl. \quad (4)$$

For eq. (4) to hold we have to assume that the molecular wire is terminated at the two ends 1 and 2 into electroactive reservoirs where the particle can be

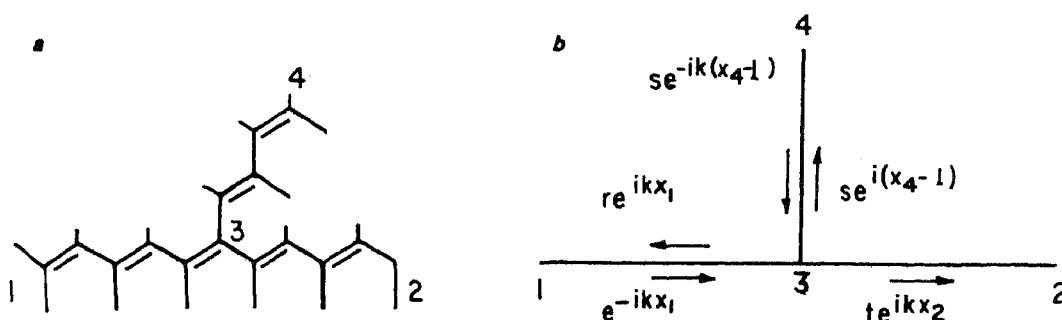


Figure 1. a, Hypothetical branched conjugated chain. b, Equivalent network showing partial wave amplitudes.

injected or removed reversibly. The expression (3) is, of course, valid generally and is central to our discussion.

As is readily seen, the transmission is resonantly tuned by the side-chain length l . Most importantly, the electron transfer can be blocked for certain tuned values of the side chain length, i.e. for $\cot kl=0$. This suggests the intriguing possibility of a critical regulation of electron transfer between sites of reduction and oxidation in a supramolecular structure. It has been suggested that long-distance electron transfers are involved in the enzyme catalysis of biological activity and, indeed, specific pathways for electron transfers have been proposed⁷. What we are suggesting here is that in such cases a critical regulation, or control of the action, can be achieved by a relatively small molecule acting as a side-chain of suitable length located on the pathway.

Finally, for this purely quantum-interferential control to be effective, a long coherence length is required at physiological temperatures. This favours the solitonic mode of charge transport along the conjugated chain.

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Occurrence of twinning and parallel growth in zircons of the Palampur granitoids, northwestern Himalaya

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Well-developed geniculate and less regular types of twinning and two types of parallel growth have been observed in zircons of the Palampur granitoids. The crystallization histories of such crystals have been deduced on the basis of morphological features. These primary growths are considered to be of magmatic origin, and have formed at a late stage in the crystallization history of zircons.

ZIRCONS sometimes show various kinds of primary and secondary growth features. The primary growths are in the form of parallel, necked and twinned crystals. Such growths are quite rare in zircons and are considered to be characteristic of magmatic granitoids^{1,2}. Secondary growths occur in the form of enhanced overgrowths, outgrowths and multiple growths. These growths are relatively common in zircons and are characteristic of anatectic or metasomatic granitoids²⁻⁶.

During investigations on Palampur granitoids⁷, well-developed twinning and parallel growths have been noticed in the zircons; these are recorded for the first time from the Himalayan granitoids. It may be mentioned that such growth features are extremely rare in the literature.

Two types of twinned zircons were observed in the rocks under study. These are: (i) the geniculate or elbow type of twinning (Figure 1a,b) with (101) or (011) as composition plane. These twins are quite comparable with British Museum (Natural History) twinned zircons as reproduced in Figure 2:9 of Jocelyn and Pidgeon¹; (ii) these crystals are of a less regular type of twins (Figure 1c-e). In this case, the zircons are no longer symmetrical about the composition plane which itself penetrates partly into the crystal. These examples of twins are comparable with Figure 1:6-9 of Jocelyn and Pidgeon¹.

The morphological outlines of the above described zircons indicate that in the case of geniculate twins, initially the crystals had separate growth histories, and later on they joined together to form geniculate twins. On the other hand, in the case of less regular twins, it seems that both the crystals had joined together at an earlier stage of crystallization, and they then grew separately to form twins. These twinned crystals therefore, are likely to have formed at a late stage in their crystallization history.

Zircons of the Palampur granitoids exhibit two types of parallel growth: (i) composite parallel grown zircons lying on face 100 and united along (100) composition plane (Figure 1f-h). Such zircons show parallel or nearly parallel extinction, as the C-axes of both the crystals are parallel; (ii) composite parallel grown zircons lying on prismatic face 110 or 100 and showing a tendency to join along a pyramidal face (Figure 1i). The plane along which such crystals are united is somewhat irregular and inclined (Figure 1j). The parallel growths have also been noted by other workers^{1,2,8,9}. Poldervaart and Eckelmann³ named such zircons as 'aggregate crystals'.

The presence of different type of morphological features, like inclusions, cracks, concentric zones, etc. in both the portions of composite zircons indicates that initially both the crystals had grown separately, and subsequently they joined together resulting in parallel growths. Jocelyn and Pidgeon¹ stated that the rarity of