

supporting the tunnel path) with the surface metallic orbitals of the contacts. The resulting extension of the metallic wavefunction of the electrode into the molecular wire may be viewed as a doping effect³⁷ without introducing states in the HOMO–LUMO gap. In the STM images of molecules adsorbed at steps, the apparent height of the molecule is a clear measure of the quality of the electronic contact with their metallic step, which acts as an electrode. This accounts for the pre-factor T_0 in the expression for the tunnel transparency and provides a quantitative criterion for optimizing the metal–molecule contact.

Intramolecular circuits can be formed without metallic pads by using molecular wires. Contrary to conventional electrical circuits, where adding one branch does not change the electronic properties of the others, any new molecular wire or branch added to a molecule effectively creates a ‘new’ molecule with a different electronic structure. Therefore, a standard circuit analysis resulting from the application of Ohm’s and Kirchhoff’s laws is inapplicable even if the design of molecular logic continues to be based on those laws⁴⁰. From elastic scattering theory, the chemical binding of two oligomers with low transparencies T_1 and T_2 in series gives a total transparency T proportional to $T_1 \times T_2$. The binding of two or more oligomers in parallel requires two auxiliary branches to form the nodes (Fig. 6). In this case and when $T < 1$ for each branch, the superposition law yields $T = T_h + T_b + 2(T_h \times T_b)^{1/2}$ (ref. 40) with T_h and T_b being the transparency of each complete individual branch (Fig. 5). However, it is not yet clear whether the invalidity of standard circuit analysis derives solely from the inapplicability of Ohm’s law, emphasizing the need for experimental investigations of intramolecular currents. Nanopore measurements on molecule 17 (Fig. 1e), which consists of three conjugated branches associated in series via two non-conjugated CH_2 nodes⁴⁰, have revealed a very small NDR effect attributed to the central phenyl ring, indicating a multiplicative rather than additive superposition for an association in series. In order to probe along each branch of an intramolecular circuit, large and multi-branched macromolecules⁴¹ need to be synthesized (and imaged), indicating that the fabrication precision

in MME can then be combined by chemical synthesis and nano-fabrication techniques, a process referred to as directed self-assembly.

Intramolecular devices will need to be controlled internally without crosstalk to adjacent molecules. Suitable intramolecular wiring and circuitry^{45,46,47} has been proposed, but an intrinsic gating effect that allows internal control has not yet been identified. Even SWCNTs crossing each other⁴³ or junctions⁴⁵ on the molecular scale are typically gated with an electrode connected to a macroscopic pad, suggesting that intramolecular electronic wavefunctions might need to be manipulated differently, such as is done in quantum computing to perform computation inside a single molecule. However, the laws governing the physics of an intramolecular circuit in the tunnelling regime are poorly known. Although it might be possible, for example, to use the vibronic pseudo-continuum associated with many electronic states of a large molecule to break microreversibility and thus design intrinsic three-terminal devices, we cannot yet test this idea directly owing to the difficulties in observing inelastic effects experimentally⁴⁴. Electron correlation effects have now been observed in MWCNTs⁴⁸ and SWCNTs⁴⁹, but further advances in this direction are required to determine whether a full mono-molecular approach is technologically viable and thus able to provide a realistic alternative to monolithic silicon devices.

Nanofabrication

The fabrication of a circuit using HME devices or the interconnects of MME devices requires the following steps: (1) fabrication of millions of multi-electrode nanojunctions with interelectrode distances down to a few nanometres; (2) wiring these junctions to interconnects; (3) deposition/assembly of one molecule or super-molecule per nanojunction; (4) fabrication of the input/output and driving power interconnects; and (5) packaging the circuit. Currently, two-electrode nanojunctions down to 5 nm have been produced by electron-beam nanolithography, and electrodeposition techniques have revealed that 2 nm can be reached (Fig. 5). Two nearby SWCNTs have also been used to define a nanojunction using

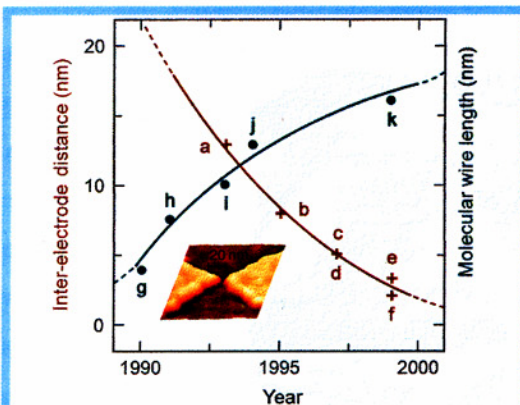


Figure 5 Variation of the inter-electrode distance of planar nanojunctions and the length of the synthesized molecular wires as a function of time. Red, inter-electrode distance; green, molecular wire length. **a**, **b**, Planar standard e-beam nanolithography nanojunctions, ref. 97 (**a**) and ref. 22 (**b**). **c**, **d**, Co-planar e-beam nanojunctions with the electrode metal at the same height as the substrate, ref. 21 (**c**) and ref. 27 (**d**). **e**, **f**, Suspended planar nanojunctions fabricated by electrodeposition¹⁰⁰ (**e**) and electrochemistry¹⁰¹ (**f**). **g**, **h**, Long oligoimide molecular lines, ref. 100 (**g**) and ref. 101 (**h**). **i**, Thiophene-ethylene oligomers¹⁰². **j**, Phenylalkyne oligomers¹⁰³. **k**, Alternating block co-oligomers of (1,4-phenylene ethynylene)s and (2,3-thiophene ethynylene)s¹⁰⁴. Inset, AFM tapping mode image of a 4-nm coplanar nanojunction. In **e**, the two gold-palladium metal electrodes are only 1 nm higher than the background silicon wafer surface²⁷.

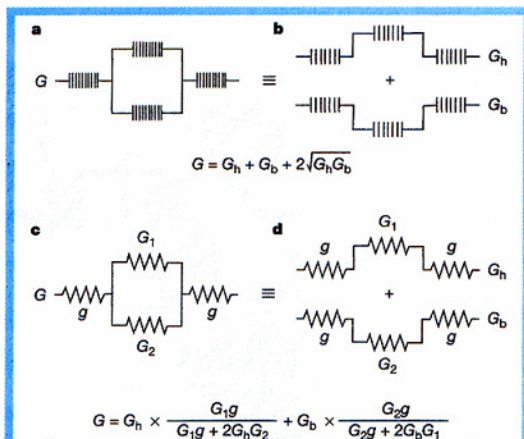


Figure 6 Illustration of the superposition rule operating in a pure tunnelling regime for a simple intramolecular circuit. **a**, The circuit is made of a molecule composed of two branches bonded in parallel and connected to the pad through molecular wires. **b**, The full conductance G of the metal–molecule–metal junction is obtained by decomposing the circuit into two parts having junction conductances G_1 and G_2 , respectively, and summing up G_1 and G_2 as indicated (the same rule applies for the transparencies). **c**, By comparison, the conductance G of the same circuit, but with conventional ohmic resistances g , G_1 and G_2 , can also be decomposed in this way (**d**). Of course, this decomposition is never used in circuits, and G for **c** is better calculated using standard circuit analysis.