conformation and the exact number of interconnected molecules remain essentially inaccessible[19]. Nevertheless, measurements have provided estimates of $R = 22\,M\Omega$ ($T = 5.9 \times 10^{-4}$) for a junction containing molecule **9** shown in Fig. 1a (ref. 18). In the case of molecule **10** (Fig. 1a) and its dimer, values of $R = 12.5\,M\Omega$ ($T = 1.03 \times 10^{-3}$) and $R = 160\,M\Omega$ ($T = 7.7 \times 10^{-5}$) were obtained, respectively[19].

Electro-deposition techniques[20] use suspended electrodes in a pseudo-planar configuration to trap molecules electrostatically in and onto the junction. Interrupting the trapping field at the first observed increase of the current in the circuit leads to the deposition of a finite number of molecules in the junction. This approach is similar to break junctions, but there are no imaging methods available to verify the actual number and orientation of the molecules in the junction. Using this configuration, an oligonucleotide straddling an 8-nm nanojunction was found to be negligibly electrically conducting up to an applied potential of several volts[24].

Nanolithography has made important contributions towards using mesoscopic electrodes[25,26] and nanojunctions for HME[27]. The measurement of the conductance of single-wall carbon nanotubes (SWCNTs) represented the observation of molecular-scale objects electrically interconnected in a full planar configuration, together with images of the position and conformation of the macromolecule[25,26]. SWCNTs with appropriate helicity were found to transport electrons ballistically[25], that is, their electronic transparency is $T = 1$. Consequently, the conductance of the metal–SWCNT–metal junction is determined by the metal–SWCNT contacts. It has generally been difficult to decrease contact resistances in these systems below 100 kΩ (ref. 28), but the use of catalysts to pattern and grow SWCNTs directly onto electrodes has recently resulted in two-terminal contact resistances as low as a few kilo-ohms (ref. 29).

At low voltages, two regimes of elastic transport explain the large scatter of transparency values measured on single molecules. (Transport can involve either electrons or quasi-particles, such as polaron and soliton carriers.) For $T > 1$, the transport regime is ballistic: the molecular levels are in resonance with the Fermi level of the electrodes, and there is complete electronic delocalization along the molecule. In the case of SWCNTs at low temperatures[30], the transport coherence length can extend to as much as 500 nm (Fig. 3). Values of $T < 1$ indicate that either the molecule is differently bound to the electrodes or that the Fermi level is located within the gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals. In the first case, the tunnelling regime is determined by the metal–molecule contact, which can be optimized by controlling the surface chemistry. To overcome the second situation, the molecular orbitals need to be electronically coupled to the electrodes to stabilize a tunnel pathway for the carriers that is more efficient than vacuum. This pathway builds up from the constructive or destructive superposition of tunnel channels. For C_{60} adsorbed on the Au(110) surface, this involves 36 of a total of 240 molecular orbitals[14]. For systems with $T < 1$ and involving a molecule symmetrically chemisorbed on the electrodes, such as C_{60} bound to two similar electrodes, two-terminal measurements exhibit linear I–V characteristics when V is much lower than the molecule's effective barrier height[14,19]. This Simmons tunnelling regime is analogous to electron tunnelling between metals at low voltages, also resulting in linear I–V curves. Nonlinear I–V curves usually occur at higher voltages in systems with $T > 1$ involving a physisorbed molecule[31,32], owing to the contact tunnel barriers at the electrodes dominating the behaviour of the system[25].

Calculations support a very fine dependency of the metal–molecule–metal junction resistance on the chemical structure of the molecule[33,34], its conformation in the junction[35], and its chemical binding to the electrodes[33,36,37]. In these calculations, the electronic and mechanical description of the junction includes the atomic structure of the electrode and the molecular conformation obtained from semi-empirical[38] or, more recently, from density-functional approaches[39]. The tunnelling current intensity is usually derived from the Landauer formula[14], with the scattering problem being solved using a spatial propagator[40] or a Lippman–Schwinger technique through its kernel (Green's function)[41]. Alternatively, the current intensity can be calculated from a time-dependent approach that relates the electron transfer process through the

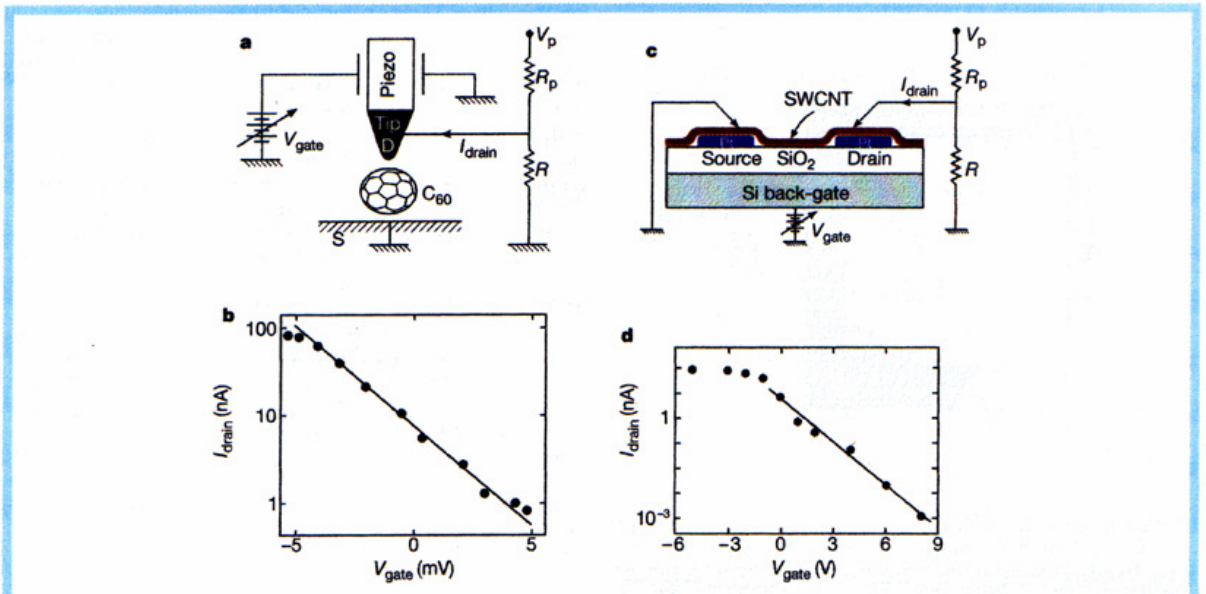

Figure 2 The first two active three-terminal devices in molecular electronics. **a**, **c**, Electrical circuits of **a**, the electromechanical single C_{60} amplifier (in its original scanning tunnelling microscope version[15]) and **c**, the single-wall carbon nanotube (SWCNT) channel transistor[53] with their respective $I_{drain} = f(V_{gate})$ characteristics (S, source; D, drain; I_{drain}, the tunnel current intensity through the molecule). From **b**, the transconductance dI_{drain}/dV_{gate} of the C_{60} amplifier is $g = 3.9 \times 10^{-6}\,AV^{-1}$ and from **d**, that of the SWCNT transistor is $g = 8 \times 10^{-9}\,AV^{-1}$. Those values must be compared to $g = 30 \times 10^{-3}\,AV^{-1}$ for a bipolar transistor and $g = 3 \times 10^{-3}\,AV^{-1}$ for a vacuum-tube triode. The channel of these HME devices (**a**, **b**) is truly molecular in scale, but not the grid.