can also emit light for monitoring processes within the junction in real-time.

A tunnel junction consists of two materials, a cathode and an anode, separated by a thin dielectric layer (Fig. 1a). When the junction is electrically biased there is a small but finite probability of electrons quantum tunnelling across the junction from the cathode to the anode. Most electrons will tunnel through the junction elastically, not losing any energy and resulting in hot electrons at the surface of the anode. At this point, the hot electrons will quickly thermalize, losing their excess energy to heat generation, and thus they must be harnessed immediately. In the rarer inelastic case, the transmitting electron will lose energy, which can result in the generation of a surface plasmon in the anode[9]. This surface plasmon can either radiate, generating light, or decay non-radiatively, resulting in additional hot electrons.

One of the main challenges involved in employing tunnel junctions for chemical reactions is maintaining a nanoscale air gap between the cathode and anode over large areas. Usually, tunnel junctions are created by oxidizing the surface of a material or growing a dielectric film using, for example, atomic layer deposition. However, the resulting architectures don't allow chemical species to access the hot electrons at the surface. A solution would be to use lithographic techniques to design planar electrodes with nanoscale gaps, but this approach is difficult to scale up. As such, the majority of past work concerned with harnessing hot carriers has focused on optical excitation of nanoparticles and nanostructures with easily accessed surfaces. However, optical excitation of hot carriers is not a particularly efficient process — if carriers generated in the bulk of the material are to be utilized, they must diffuse to the surface before thermalizing.

In their report, Wang et al. detail a tunnel junction-based metamaterial fabricated using gold nanowires that are embedded in, and templated by, self-organized nanoporous anodic aluminium oxide membranes. Using electroplating to grow the nanowires, followed by ion milling, the authors are able to create a nanometre-scale gap between the top of the wire and the top of the membrane. This enables two configurations. First, if the nanowire surface is left below the surface of the aluminium oxide, air gaps can be formed which act as the tunnelling barrier (Fig. 1b). Second, if the nanowires are exposed, they can be coated with a monolayer of molecules which serve as the tunnelling barrier while preserving a small air passage that allows for diffusion of chemical species to and from the junction area (Fig. 1c). In both cases, a top electrode is formed using an eutectic liquid-metal (E-GaIn), which ensures contact with the top of the wires, or assembled monolayer, over a large sample area. The devices operate with the eutectic liquid serving as the cathode and injecting electrons into the nanowire. More than 99% of these electrons transmit through the junction elastically as hot carriers, resulting in the tops of the nanowires being extremely reactive. Some of the remaining inelastically transmitted carriers generate surface plasmons in the gold nanowires, which then serve as antennae, radiating light into free space.

The researchers demonstrate that upon electrical biasing, the structure radiates red light corresponding to the surface plasmon resonant frequency of the gold nanowires. Impressively, this light emission is observed over a 4 mm² area, or across nearly 10[11] tunnel junctions. Although this is not an efficient light emission process, the emitted intensity is affected by the composition of the tunnel junction and thus serves as a real-time indicator of the chemical processes there. Due to the extremely reactive nature of hot electrons, the researchers observe compositional changes in the monolayer-coated junctions when particular gases are introduced into the metamaterial. These changes can be observed in both the magnitude of the tunnelling current and light emission from the material. They hypothesize that this is due to oxidation and reduction reactions, though further studies will be needed to elucidate the exact changes occurring in the junction. One other potential direction of future work could be to increase diffusion rates of species to the junctions, as this is a factor that limits response time in the current configuration.

Compared to hot-electron generation using optical excitation, the use of tunnel junctions is a much more efficient process as nearly every transmitted electron results in a hot carrier. Furthermore, these hot carriers are generated directly at the surface of the anode, increasing the likelihood of reactions occurring before thermalization. Combined with the convenience of external electrical control, these benefits result in an attractive platform for monitoring chemical reactions, sensing trace gases and studying fundamental optoelectronic processes at the nanoscale; tunnelling-based devices for optoelectronic applications can also be envisaged. ❑

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MOLECULAR JUNCTION REFRIGERATOR

Peltier cooling at molecular scale

Under specific conditions, molecular monolayers dissipate power more than they heat up at one end of a molecular junction, validating theoretical predictions of Peltier cooling.

Keehoon Kang and Takhee Lee

The increasing demand for miniaturization of electronic devices has resulted in extensive research into molecular components that can be incorporated into active elements in nanoscale devices[1]. In principle, the concept of tailoring the electronic, optical and thermal functionalities of molecules by chemical synthesis is an attractive
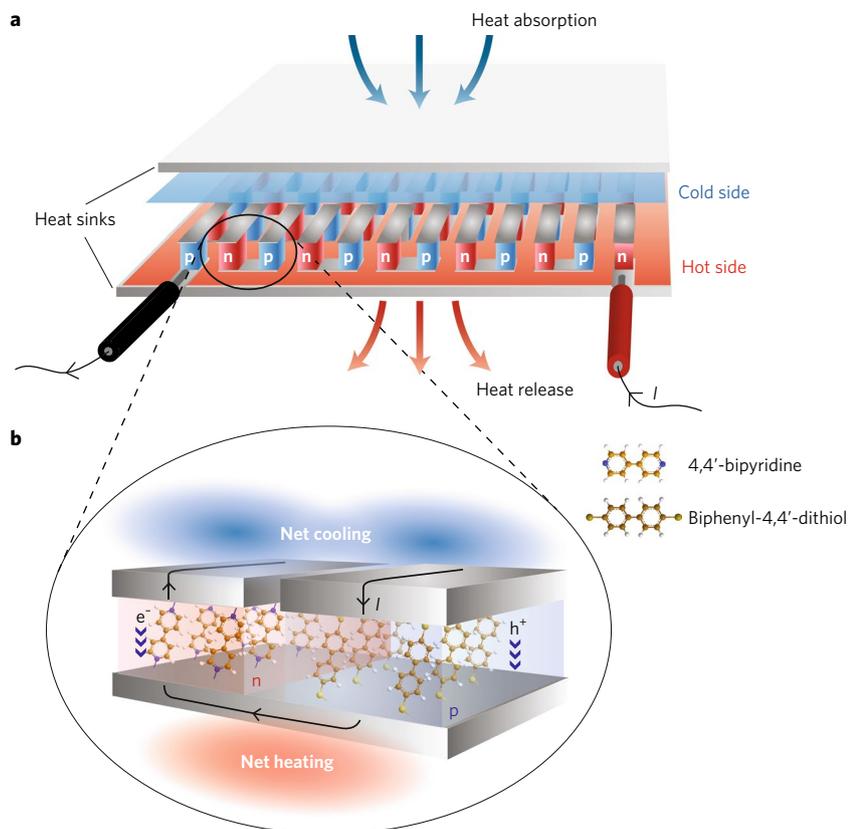
Fig. 1 | Conventional and molecular-scale Peltier coolers. a, A schematic diagram showing a conventional thermoelectric generator (Peltier cooler) in an array structure of repeated cells consisting of vertically stacked n-type (red) and p-type (blue) semiconductor layers electrically connected by metal interconnects to form a circuit. The whole layer is sandwiched between two heat sinks where the heat exchange occurs with the surroundings. In this specific configuration, where a steady-state current, I, flows in the direction as shown, the top surface becomes cold (shown in blue) and the bottom surface becomes hot (shown in red). **b**, A conceptual design of a thermoelectric cell for a Peltier cooler made of molecular junctions with molecules studied by Cui et al.[3]. The conduction in 4,4′-bipyridine is dominated by LUMO and biphenyl-4,4′-dithiol by HOMO, and therefore these molecules can replace n- and p-type semiconductors, respectively, to result in a net cooling at the top surface and a net heating at the bottom.

proposition for fabricating molecular devices that fit one's needs. In particular, research on thermoelectric effects in molecular junctions has recently attracted a tremendous amount of attention owing to the predicted large thermopower and thermoelectric power conversion efficiency of molecules[2]. The goal is to develop technologies that can harness dissipated thermal energies from the surroundings and convert this into useful work, in the form of electrical energy. Reporting in *Nature Nanotechnology*, Cui et al. now describe the experimental observation of Peltier cooling — that is, refrigeration — in molecular junctions[3].

The Peltier effect refers to the reversible absorption or liberation of heat at the junction of two materials depending on the direction of a current, I, flowing through the junction (Fig. 1a). One main

component of the heat exchange at the junction of two materials is the irreversible heat dissipation (Joule heating) which has the form $Q_J = IR^2$, where R is the junction resistance. Joule heating has been recently observed down to the atomic scale[4]. Another component is the reversible heat exchange due to the Peltier effect, which has the form $Q_P = \Pi I$, where Π is the Peltier coefficient. One important aspect of the Peltier effect is that the direction of the heat exchange at the junction (that is, heating or cooling) can be controlled by switching the current direction. The Peltier effect has been used for solid-state cooling to avoid electronic device degradation due to excess temperature rise. A conventional architecture used for such devices is shown in Fig. 1a. Microscopically, Peltier cooling occurs by means of charge carriers (electrons in an n-type semiconductor) that carry away

some heat from the metal–semiconductor junction when they are thermally excited into the conduction band (again, for n-type semiconductors). This extra heat is then carried through the semiconductor and released at the other junction.

Although local cooling in electrically biased molecular junctions was predicted theoretically several years ago[5], experimental validation remained challenging, even though its reciprocal counterpart, the Seebeck effect, in which an electric field is generated along an applied thermal gradient, has been previously observed in molecular junctions[6–8]. It seemed only a matter of time before the Peltier effect could be measured as well. In fact, the effects are two faces of the same coin and can be related by the Thomson relation, $\Pi = TS$, where S is the Seebeck coefficient and T is the temperature of the junction. From this relation and a molecular version of Q_P ($Q_P = \Pi GV$, where V is the applied voltage, and G the molecular conductance), we can understand the underlying challenges in measuring the Peltier effect in molecular junctions: the order of magnitude of the heating or cooling power is tiny (in the picowatt range), considering the experimentally determined values of $S \approx 10\ \mu VK^{-1}$, $G \approx 0.01\,G_0$, where G_0 is the conductance quantum, and $T = 300$ K. Therefore, despite the great interest in using molecular junctions for achieving refrigeration, the experimental observation of Peltier cooling through direct calorimetric measurement has remained inaccessible.

Cui et al. have managed to custom-build a picowatt-sensitive calorimeter by using a microdevice incorporating platinum stripe thermometers that are electrically insulated from but thermally connected to a gold layer on which self-assembled monolayer molecules have been deposited. A conducting-probe atomic force microscope composed of a gold-coated cantilever tip can make a soft contact with the molecules on the microdevice to complete the junction. The combined device architecture forms a multi-functional platform that is suitable for simultaneously measuring the electrical conductance, the Seebeck coefficient and the total heat absorbed or dissipated at the junction, Q_{tot}, under a bias voltage applied at the probe. The resolution of the heating or cooling power that can be detected is around 30 pW, more than enough for the maximum cooling power, $Q_{tot} = 300$ pW, measured in the study for biphenyl-4,4′-dithiol monolayers (Fig. 1b). It is important to note that the measured Q_{tot} contains contributions from both Q_J and Q_P; its value is therefore modulated by (i) the magnitude and polarity of the bias voltage and (ii) the relative position of the molecule's frontier orbital

energy level with respect to the Fermi levels of the electrodes. Indeed, the researchers observe switching from cooling to heating when they reverse the bias voltage, and there exists a bias voltage value at which the net cooling effect is maximized. This behaviour can be interpreted as a competition between the Q_J and Q_p terms. The same switching occurs when the molecules in the molecular junctions are switched from biphenyl-4,4′-dithiol to 4,4′-bipyridine, in which the carrier tunnelling occurs mainly in the lowest unoccupied molecular orbital (LUMO), rather than the highest occupied molecular orbital (HOMO) (that is, Π switches from positive to negative).

From a theoretical point of view, one needs to take into account the quantum-mechanical nature of Q_{tot} in the charge transport and introduce the Landauer formalism in which the transport is dictated by an energy-dependent transmission probability spectrum of the molecules in the junction. Cui et al. validate their experimental results by computing the transmission probabilities for the three

investigated molecules, and confirm that the switching of Q_{tot} from heating to cooling for biphenyl-4,4′-dithiol and 4,4′-bipyridine arises from the conduction in the HOMO and LUMO, respectively.

The molecular-scale Peltier effect observed by Cui et al. may not be of immediate practical relevance. But one could optimize the thermoelectric energy conversion efficiency, which would boost Π, using molecules that have been predicted to have greater thermoelectric figure-of-merit due to quantum interference effects in the molecular transport[2,9]. Subsequently, one could envisage integrating these molecular junctions in a dense array to increase the total power output — that is, the refrigerating power (Fig. 1b). However, this conventional array structure is far from an ideal design for refrigeration for molecular junctions, because it would be challenging to maintain a large temperature difference in nanoscale gaps, owing to considerable thermal conduction through the molecules; such heat flow would introduce a lossy channel for the hypothetical molecular

junction cooling devices. Although the work of Cui et al. is an important first step, many advances and optimizations are needed before thinking of any practical implication. ❑

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TWO-DIMENSIONAL MATERIALS

Tunable confinement of charges and excitations

Electrical control over quantum confinement opens a new avenue for spatial manipulation of charge carriers and bound excited states for quantum opto-electronics.

Deep Jariwala

Two-dimensional (2D) semiconductors that can be isolated from van der Waals layered materials such as the transition metal dichalcogenides (TMDCs) provide a unique material system for opto-electronics and condensed-matter physics. The structural and electronic confinement in two dimensions brings with it several new physical properties, such as a transition from indirect to direct bandgap upon isolation from bulk to monolayer, and strongly bound excitons that are stable up to room temperature[1,2]. These properties have enabled the demonstration of atomically thin electronic and photonic components[3,4]. But one of the most promising features of 2D van der Waals materials is their ability to be tuned electrostatically. These properties, in combination, give rise to new physical phenomena and applications that are difficult to achieve in other quantum material systems.

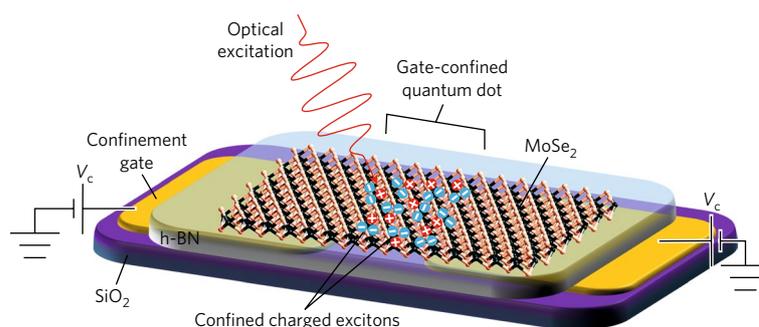Writing in *Nature Nanotechnology*, Wang et al.[5] have made a critical advance

Fig. 1 | Schematic of a gate-defined monolayer MoSe$_2$ quantum-dot device, with negatively charged excitons localized in the gate-confined region. h-BN, hexagonal boron nitride.

in using electrostatic tuning to induce 0D quantum confinement within the 2D plane of ultrathin MoS$_2$ and MoSe$_2$. Using nanofabricated metallic electrostatic gates, the authors have achieved spatial variation of the potential at a length scale of 50 nm, enabling the formation of quantum dots.

Even though quantum confinement in electrostatically gated TMDCs has been reported before, their work demonstrates several developments in fabrication and contact engineering, yielding high-quality samples with mean free paths of around 100 nm for the carriers. As a result, the