

quality of the measurement of $F(x,y,z)$ was good enough to further recognize that the interfacial water adopts the form of a double layer. Interestingly, whereas one layer shows hardly any structure, the other layer, which is closer to the mica surface, exhibits a periodic structural pattern fully in line with the crystal-lattice structure of the underlying mica.

Fukuma and colleagues' observations¹ are of particular relevance in view of the ongoing debate about whether water is solid-like^{6,7} or liquid-like⁸ near a solid surface such as mica. Discovering the exact nature of interfacial water is important because solid–water interfaces are ubiquitous in nature and have a critical role in many biophysical and technological processes. The authors' results show that interfacial water can actually combine both solid-like and liquid-like aspects, and so offer a possible reconciliation between the seemingly conflicting evidence^{6–8} that has been acquired using techniques other than 3D-AFM. One point that remains to be addressed is the influence that the tip may have on the structure of the water close to it⁷. Even in a solid-like water layer, the molecules will have sufficient mobility to respond and adjust fully to the presence of the tip.

We can envisage several instrumental improvements to Fukuma and colleagues' 3D-AFM. Smaller cantilevers^{9,10} than those used by the authors¹ have the potential to

significantly improve the signal-to-noise ratio of the measurements. Faster electronics could also be used to reduce the image acquisition time. These and other improvements to the 3D-AFM may soon allow investigations of subjects other than water–mica interfaces, such as hydration layers covering hydrophobic surfaces^{11,12} and bilipid membranes¹³, and the hydration shells surrounding ions adsorbed to surfaces, individual protein molecules and colloidal particles. ■

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50 YEARS AGO

'Tizard and the Science of War'
— His flair for setting the cat among the official pigeons, and for ignoring the normal channels, made him not always popular with the upper hierarchy. His sharp incisive wit was often exercised at the expense of the complacent, the pompous and the incompetent ... but I never heard of it being used at the expense of the young, the vigorous or the keen. There is a story which shows his ready wit, dating from the meeting of the British Association in Canada before the War. Tizard and a colleague inadvertently crossed over into the United States near Niagara. When challenged by a policeman, and not having their passports with them, they produced their Association membership cards. When the policeman told them that "The American Government doesn't recognize British Science", the lightning reply came from Tizard, "Oh, that's all right, neither does the British Government". P. M. S. Blackett
From *Nature* 5 March 1960.

100 YEARS AGO

In the course of some experiments on the phosphorescence of minerals ... it was suggested to me by Prof. Strutt that it would be of interest to examine the spectrum of the light from luminous bacteria. Through the kindness of Sir James Dewar, Prof. Strutt was enabled to furnish me with a dish containing bacteria produced from fish, which when viewed in a darkened room, were seen to glow with a greenish-blue light bright enough to enable one to read a watch ... The light emitted by the bacteria consisted of a continuous spectrum extending from wave-length 5000 ... to wave-length 3500 tenth-meters ... The photographs I have obtained indicate that in some cases these bacteria emit ultra-violet radiation, and I hope with another spectroscope, now in course of construction, to obtain more definite information. R. W. Forsyth
From *Nature* 3 March 1910.

MATERIALS SCIENCE

Hydrocarbon superconductors

Matthew J. Rosseinsky and Kosmas Prassides

Superconductivity has been discovered in the materials that form when alkali metals react with a solid hydrocarbon. This is the first new class of organic, high-temperature superconductor in a decade.

Hydrocarbons are essential to everyday life — for example, the saturated hydrocarbons known as alkanes are prime constituents of fuels such as petrol. Most people, however, wouldn't think of hydrocarbons as being electrically interesting. But on page 76 of this issue, Mitsuhashi and colleagues¹ challenge this preconception with their report of superconductors that are based on a hydrocarbon called picene. These small-molecule-based materials open up new avenues for research into superconductivity.

The carbon and hydrogen atoms in alkanes are connected by single bonds (σ -bonds), within which electrons are tightly bound and so are unable to conduct electricity. But unsaturated hydrocarbons contain some double or triple bonds between carbon atoms. These multiple bonds consist of a σ -bond and one or two π -bonds, within which electrons are less tightly bound than in σ -bonds. Such π -electrons can

take part in electronic conduction and optical processes, thus forming the basis of organic electronics, which find applications in displays, lighting and solar cells².

Molecules possessing extensive systems of π -bonds were the main components of the first molecular superconductors (in which the basic building units of the extended solid structure are molecules, rather than atoms as in metals or alloys, or ions as in ceramics); however, the charge-carrying electrons were largely derived from sulphur or selenium atoms, rather than from carbon atoms³. Simple organic molecular solids alone can also become superconductors under high pressure⁴, but again, these contain other elements in addition to carbon (such as iodine or oxygen).

Superconductivity based purely on π -electrons from carbon atoms was first observed in KC_8 — graphite in which potassium atoms have been inserted (intercalated) between

50 & 100 YEARS AGO

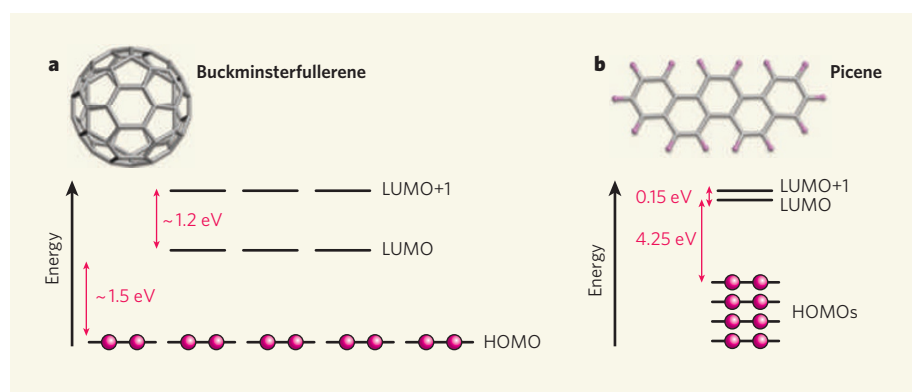


Figure 1 | Electronic structures of selected π -electron-containing systems. When alkali-metal (A) atoms are doped into solid buckminsterfullerene (C_{60}), the resulting material A_3C_{60} is a superconductor. Mitsuhashi and colleagues¹ report that the hydrocarbon picene ($C_{22}H_{14}$) is also a superconductor when doped with alkali metals. Comparison of the ‘frontier molecular orbitals’ — the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) — of picene and buckminsterfullerene reveals similarities. **a**, The LUMO for buckminsterfullerene is triply degenerate: it consists of three orbitals of equal energy. Alkali-metal atoms doped into buckminsterfullerene donate electrons to the molecule’s LUMO, and generate the necessary charge carriers for metallic conduction. When the LUMO is half-full, the resulting material is a superconductor. Red dots represent electrons; LUMO+1 is the second-lowest unoccupied molecular orbital. **b**, In picene, LUMO and LUMO+1 are almost equivalent in energy, creating an accidental double degeneracy. Superconducting charge carriers are also generated in picene when these orbitals accept electrons from alkali metals doped into the compound. The degeneracy (or pseudo-degeneracy) of the electron-accepting orbitals in buckminsterfullerene and picene is crucial for generating a high density of electronic states at the Fermi level of these solids, raising the temperature below which the materials superconduct, and might be a link between the electronic structures of the two classes of superconductor.

the flat layers of carbon atoms. The transition temperature (T_c) below which KC_8 becomes a superconductor is 0.125 K, but this has been brought up to 11 K for a related material, CaC_6 , in which calcium atoms replace the potassium atoms⁵. Intercalation of alkali metals into solid buckminsterfullerene (C_{60}) yields materials that have a higher T_c than the graphite compounds — up to 38 K for Cs_3C_{60} (ref. 6). These materials adopt three-dimensional, highly symmetrical structures owing to the spherical shape of C_{60} .

Mitsuhashi and co-workers¹ now report that alkali metals intercalate into the crystal lattice of the hydrocarbon picene to form superconductors that have T_c values of up to 18 K. This is the first example of a molecular superconductor in which the organic component contains only carbon and hydrogen atoms. Picene ($C_{22}H_{14}$; Fig. 1) consists of five benzene rings fused together along their edges, and is a flat molecule. It is therefore more reminiscent of a small fragment of a single sheet of graphite, rather than a three-dimensional C_{60} molecule. This planarity is imposed on picene by the overlap of π -electrons throughout the molecule.

The authors¹ made their superconductors by reacting alkali-metal vapour with solid picene. The interactions between the molecules in picene crystals are weak, allowing alkali-metal atoms to enter the lattice by increasing the spacing between the molecules. The existence of low-lying, unoccupied π -electronic states in picene allows the molecule to accept electrons from the alkali metals, thus generating

the charge carriers required for superconductivity — this is the same mechanism of charge-carrier generation as is found in the metal-doped graphite and C_{60} compounds.

To understand how picene-based materials compare with other families of π -electron-based superconductors, it is important to consider the nature of the orbitals accepting the electrons. The highly symmetrical nature of C_{60} makes its electron-accepting orbital triply degenerate — there are three orbitals of the same energy (Fig. 1). In picene, degeneracy is impossible because the symmetry of the molecule is too low. It is therefore interesting that Mitsuhashi and colleagues’ calculations¹ show that the two lowest-energy orbitals in picene have almost the same energy, creating an accidental degeneracy, and thus a possible link to the electronic structure of the C_{60} systems.

So what is the molecular structure and composition of the superconducting phase in metal-doped picene? The number of metal atoms per picene molecule controls the number of electrons donated to the hydrocarbon, and thus determines how many electrons fill the lowest-energy orbitals to become possible charge carriers. Considering the electronic structure of picene, it seems that up to four electrons could be accepted by the molecule’s pseudo-degenerate lowest-energy empty orbitals (Fig. 1); if two electrons were accepted, the resulting state would be analogous to the half-full states of superconducting C_{60} systems that have accepted three electrons (the three degenerate orbitals of C_{60} can accept up to six electrons).

The packing of picene molecules in Mitsuhashi and colleagues’ superconductors will determine the paths that charge-carrying electrons take, and in particular how strongly localized they are (localization would reduce electron mobility). In general, the weak interactions between picene molecules would be expected to make the conduction bands for electrons rather narrow, potentially stabilizing insulating states (such as charge- or spin-density waves, or Mott–Hubbard states) that could form in competition with the observed superconducting state. But structural information about the superconducting phase is currently lacking — it is not clear, for example, if this phase is crystalline or amorphous. It is also possible that unpaired electrons on different picene molecules pair up to form carbon–carbon bonds, thus linking the molecules together to form small oligomeric or polymeric units; such a process has been observed⁷ in certain C_{60} compounds.

When new families of superconductors are discovered, there is always much interest in the mechanism that allows the formation of Cooper pairs of electrons (the charge carriers of supercurrents), a process in which repulsion between negatively charged electrons must be overcome. In most theories of superconductivity, it is the density of electronic states at the Fermi level (the maximum energy for occupied electronic states in a metal) that sensitively controls T_c . The expected weak overlap between the outer orbitals of the molecules in the picene materials should lead to a high density of electronic states at the Fermi level, which might in part explain why their observed T_c values¹ are relatively high.

The occurrence of magnetically ordered states near the superconducting phases of certain classes of high-temperature superconductors — the copper oxides⁸ ($T_c \leq 155$ K) and the iron oxyarsenides⁹ ($T_c \leq 55$ K) — suggests that magnetism, or the repulsive electron–electron interactions that lead to it, has a central role in the Cooper-pairing mechanisms of these compounds. Recent work¹⁰ shows that such magnetic order occurs near the superconducting state of the fullerene superconductor Cs_3C_{60} , suggesting that the role of magnetism in the picene-based systems¹ should also be carefully explored. But this investigation must wait until the complex task of identifying the structure and composition of the superconducting phase has been achieved.

Mitsuhashi and co-workers¹ have unveiled an unanticipated group of molecular superconductors that seems to have a surprisingly simple chemical constitution. This is exciting news for superconductivity researchers, and should stimulate extensive work on the electronic properties of other acenes (the family of aromatic compounds to which picene belongs), because the molecular-orbital energies and packing patterns of these compounds can be systematically tuned to differ from those in picene. If superconductivity can be induced by

chemically doping other acenes, this raises the prospect of producing a broad class of superconductor that has properties as exciting as those of their π -electron antecedents. ■

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CLINICAL IMMUNOLOGY

Culprits with evolutionary ties

Carolyn S. Calfee and Michael A. Matthay

The cellular organelles we know as mitochondria are thought to have originated as symbiotic bacteria. Indeed, the two use common mechanisms to trigger innate immune responses to injury and infection, respectively.

Serious physical injury, or trauma, is a major cause of morbidity and mortality worldwide¹. Patients who survive the initial trauma, through medical and surgical interventions, often remain critically ill. One life-threatening post-traumatic complication is the systemic inflammatory response syndrome (SIRS), which is characterized by shock and compromised function of several organs. Clinically, symptoms of post-traumatic SIRS include fever, increased heart rate and low blood pressure (shock) — complications that also occur during the systemic inflammatory response to severe infection, known as sepsis. The molecular mechanism that underlies the development of SIRS after trauma and the cause of the similarity between post-traumatic and septic SIRS have been poorly understood. In this issue, Zhang *et al.*² report on one of the pathways that triggers trauma-associated SIRS and link it to pathways implicated in sepsis-associated SIRS (see page 104).

Given the similarities between post-traumatic SIRS and the host response to overwhelming sepsis, it was previously proposed that SIRS develops after trauma as a result of bacterial translocation from the bowel to the blood (due to lowered blood pressure and the subsequent poor perfusion of the bowel). However, this theory was later disproved³. More recent theories posit that the innate immune system and its pattern-recognition receptors are the main components of the common molecular pathway leading to SIRS in both infectious and non-infectious settings⁴.

In patients with severe infection, the innate immune system responds to a set of evolutionarily conserved molecules known as pathogen-associated molecular patterns (PAMPs), which are expressed by a variety of pathogens. Native molecules released after tissue injury — and therefore called damage-associated molecular

patterns (DAMPs) — can act through signalling pathways shared with PAMPs, initiating a similar innate immune response even in the absence of microbial infection⁵. Recent work has demonstrated that some DAMPs — including HMGB1 and S100 proteins — are rapidly released into the blood of severely injured patients, and elevated levels of HMGB1 in the blood have been linked to the development of organ failure after trauma⁶. Nonetheless, the evolutionary links between the signalling pathways that are triggered by PAMPs and DAMPs have not been clearly identified.

Mitochondria provide a potential link between internal and external triggers of the innate immune response, particularly given the evidence that these organelles originated from bacteria and initially lived as intracellular symbionts in eukaryotic cells (such as those of plants and animals). Indeed, mitochondrial DNA and bacterial DNA share many similar structural motifs⁷. Zhang *et al.*² therefore hypothesized that intra-mitochondrial components, including mitochondrial DNA, may act as DAMPs, triggering the same pathways that respond to PAMPs and perhaps partly explaining the similarities between the immune response to trauma and to overwhelming infection.

The authors report that severe trauma in humans causes a rapid release of mitochondrial DNA into the circulating blood, probably secondary to the tissue necrosis caused by the extensive force of the injury. Moreover, they show that mitochondrial DAMPs such as formyl peptide attract neutrophils, a type of white blood cell, as part of the initial response of the innate immune system. These molecular stimuli also activate neutrophils through formyl peptide receptor-1 on their surface, and promote a neutrophil-mediated inflammatory response through release of the immune mediators MMP-8 and IL-8 and phosphorylation

of several MAP kinase enzymes (Fig. 1).

Mitochondrial DNA could also activate p38 MAP kinase by binding to toll-like receptor-9 (TLR9) on the surface of neutrophils — an interaction that could be blocked using DNA sequences that bind to the portions of mitochondrial DNA that closely resemble bacterial DNA. But perhaps the most important observation Zhang *et al.* make is that intravenous injection of mitochondrial DAMPs into rats causes acute lung injury, which is a major cause of respiratory failure in critically ill patients⁸. Acute lung injury is characterized by protein-rich pulmonary oedema (swelling), accumulation of large numbers of neutrophils in the lungs and high concentrations of pro-inflammatory cytokines, including IL-6 and tumour-necrosis factor- α . Although the lung injury induced by DAMPs was not severe, it may act as a priming stimulus that then promotes additional lung injury after exposure to further inflammatory stimuli, such as blood transfusion or

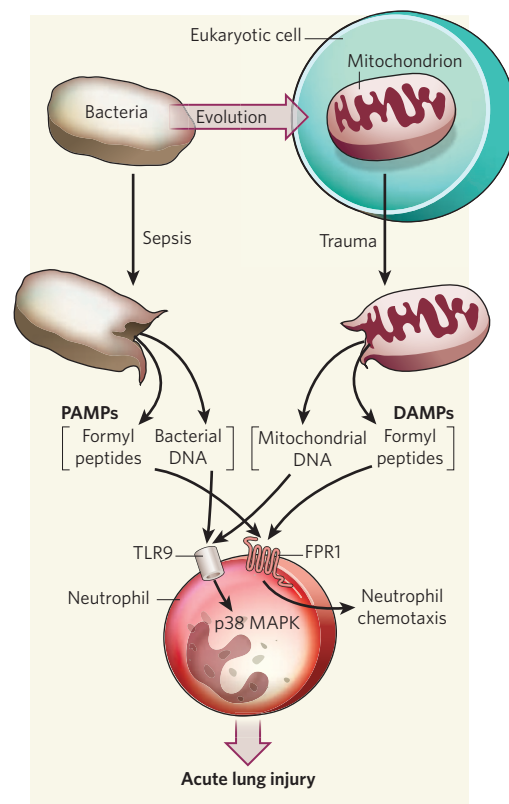


Figure 1 | PAMPs, DAMPs and the inflammatory response. Zhang *et al.*² find that, like bacterial DNA released following sepsis, mitochondrial DNA released by severe trauma can also act through toll-like receptor-9 (TLR9) to activate neutrophils through activation of p38 MAP kinase (MAPK) enzyme. Similarly, formylated peptides released from bacteria and mitochondria in these settings attract neutrophils by the process of chemotaxis to sites of inflammation and injury through formyl peptide receptor-1 (FPR1). In both cases, the outcome may be acute lung injury, as part of the systemic inflammatory response syndrome (SIRS). DAMPs, damage-associated molecular patterns; PAMPs, pathogen-associated molecular patterns.