Hydrogen bonding

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The Jekyll-and-Hyde electron transfer chemistry of hydrogen bonds

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Hydrogen bonds get a bad rap in electronic materials because their weak, transient structure often results in poor performance. Now, this dogma has been turned on its head by intercalating molecules into two-dimensional superlattices to generate hydrogen-bonded organic–inorganic structures that feature significantly enhanced electrical conductivity.

Molecular materials with controllable electronic and structural properties are of great interest for information processing and environmental sensing applications due to their low cost and facile processing[1]. They offer a vast parameter space of tuneable properties to meet higher efficiencies and lower costs demanded by the industry. Numerous applications for such materials involve resistive switching, in which the material undergoes a massive change in electrical conductivity. This typically requires a physical stimulus, such as an external electric field[2], temperature[3], pressure, or chemical-induced molecular compression[2]. A classic example is the field-effect transistor, which exhibits a robust electric field response in molecular systems[4–6]. Inducing phase transitions or chemical reactions can also be used to alter properties significantly because they produce distinct electronic structures[7].

Such electronic and structural properties in molecular materials rely on the molecules' covalent bonds and noncovalent interactions. Hydrogen bonds are relatively weak but can induce phase transitions in flexible and dynamic systems such as fluids, organic polymers, peptides, nucleic acids and proteins. However, structural fluctuations resulting from forming or breaking hydrogen bonds generally lower the conductivity, whereas high electrical conductivities typically require a very rigid structure. Therefore, it seems unlikely that hydrogen bonds can enhance electrical conductivity. Now writing in *Nature Chemistry*, Xie and colleagues defy this dogma by systematically and continuously varying the electrical conductivity of a semiconductor superlattice over a range of seven orders of magnitude using hydrogen bonds[8].

While synthetic molecular materials typically show little change in conductivity resulting from hydrogen bonding, biomolecular electronic materials have pioneered this domain. For example, in proton-coupled electron transfer reactions, hydrogen bonding networks control the availability of proton donors and acceptors, influencing molecular reduction potentials[9]. In addition, cooling stabilizes hydrogen bonds in amyloid peptides, accelerating electron transport 200-fold by aligning the molecular reduction potentials with the Fermi level of electrodes[10]. Hydrogen bonds also accelerate electron transport by changing the protein structure[2,11]. For example, common soil bacteria *Geobacter sulfurreducens* transfer electrons to extracellular acceptors using cytochrome nanowires with stacked haems[11,12]. Cooling-induced restructuring of hydrogen bonds accelerates electron transport by 300-fold by changing the haem reduction potentials[3]. Cytochrome nanowires in biofilms show ultrahigh electron and proton mobility (>0.25 $cm^2 V s^{-1}$), owing to directional charge migration through stacked haems and a charged hydrogen bonding surface, respectively[5]. Cooling increases hydrogen bond connectivity, which halves the activation energy for charge transport. As such, the extension of conductivity dependent on hydrogen bonding to synthetic molecular materials, as demonstrated by Xie and colleagues, offers an exciting peek into an unexplored landscape.

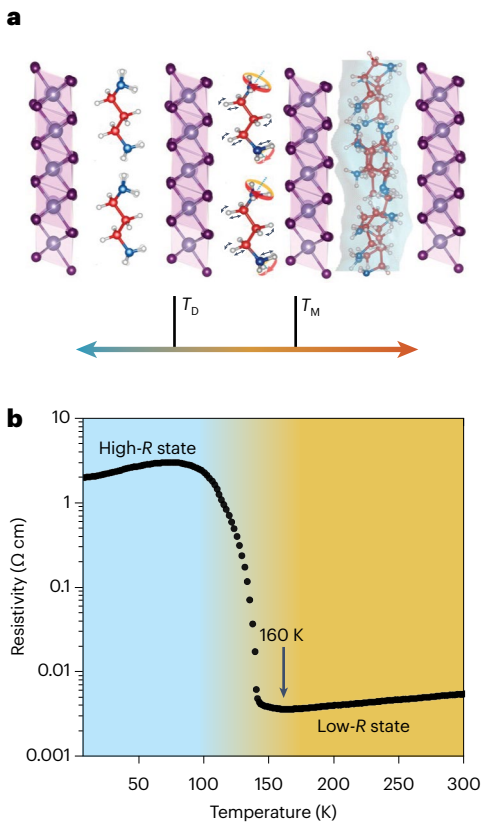

Fig. 1 | Cooling switches dynamic hydrogen bonds into static structures, thus suppressing electron transport. a, Intermolecular (T_M) and intramolecular (T_D) motions of the DAP molecules confined within $SnSe_2$ layers. **b**, Temperature-dependent resistivity (R) of $(DAP)_{0.5}SnSe_2$.

The researchers examined hydrogen bonding in a synthetic molecular material by sandwiching a small organic molecule 1,3-diaminopropane (DAP) between layers of a crystalline tin selenide semiconductor ($SnSe_2$). The molecule forms hydrogen bonds with the

electronegative selenium atoms (Fig. 1a,b). The bonding mixes the electrons from the organic molecule with the semiconductor's electrons, effectively creating a bridge to cross the material at otherwise inaccessible energies. Dynamic thermal fluctuations of the molecule cause the hydrogen bonds to break and reform in new configurations, creating new bridges for the electrons to cross. At low temperatures, the molecules freeze into one configuration, limiting the accessible paths for electrons to traverse the two-dimensional planes. However, at elevated temperatures, the thermal fluctuations promote an ensemble of configurations instead of lowering the conductivity, opening new channels for the electrons and inducing a highly stable metal–insulator transition.

Most metal–insulator transitions involve first-order phase transitions through modifications in chemical bonds that require heat exchange. As a result, energy is lost, which can be observed as hysteresis in temperature dependence measurements. The authors demonstrate that the hydrogen bonding switch in the $SnSe_2$ DAP superlattice lacks hysteresis, thus demonstrating minimal energy consumption during the hydrogen bonding transition. This offers a potential advantage over prior metal–insulator transition materials, which require energy input for resistivity switching. Xie and colleagues comprehensively establish the switching of dynamic hydrogen bonds into static structures to suppress conductivity through complementary electrical resistivity, magnetic susceptibility and heat capacity measurements. They support their data with a mechanistic model where thermally activated transitions in the positions of the amino groups of the DAP facilitated transient hydrogen bonds with the Se atoms in the host lattice. Molecular dynamics simulations show that the transition of amino ($-NH_2$) groups' free rotation to fixed angles and the formation of hydrogen bonds with adjacent Se anions excites electrons from the molecule to the host $SnSe_2$ lattice. Periodic density functional theory calculations of the superlattice reveal that the nitrogen atoms donate electron density at the Fermi level, creating transiently delocalized states that enable metallic conduction. This change in the electron distribution is temperature dependent. Moreover, replacing S with Se changes the temperature for the metal–insulator transition from 160 K to 280 K.

The work of Xie and colleagues thus elegantly manipulates semiconductors' electronic properties by forming hydrogen bonds with intercalating organic molecules. The implications of this research could extend beyond the resistivity switching demonstrated. For example, because intercalated layer materials can exhibit superconductivity[13], other molecules intercalated in superlattices could yield higher conductivity. Intercalating molecules in cytochromes to control hydrogen bonds could further enhance these biological nanowires' electrical and optical properties[14].

Also, the layering of the semiconductor with organic molecules introduces new energy states in the semiconductor's bandgap, which can profoundly impact the material's response to light[15]. In a photoelectrochemical cell, these states may preferentially localize photoexcited electrons or holes, thus altering charge separation efficiency. This is critical for generating photovoltage (for solar cells) or photochemical conversion (for the generation of solar fuels).

One can imagine a whole series of materials, mixing and matching semiconductors with hydrogen bonding molecules to hone in on the optimal conditions for efficient photoconversion. Thus, hydrogen-bonded semiconductor superlattices represent a new class of tuneable materials that may prove critical to the global energy transformation. As hydrogen bonds are widespread in diverse materials, similar approaches to alter their dynamics could yield novel electronic and optical properties in soft materials.

Altogether, Xie and colleagues' research shows a bright future for molecular systems, both synthetic and biological, in leveraging hydrogen bonds' energy efficiency, biocompatibility and high performance to engineer unusual properties.

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Competing interests

The authors declare no competing interests.