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Single-molecule devices reveal step-by-step dynamics of hydrogen bonds

Lifa Ni[1], Dong Xiang[1*] & Takhee Lee[2]

[1]*Tianjin Key Laboratory of Optoelectronic Sensor and Sensing Network Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, China;*
[2]*Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea*

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Intermolecular interactions, including hydrogen bonding, hydrophobic interactions, halogen bonding etc., are ubiquitous in nature, which play key roles in the basic chemical, physical and biochemical process of life. Among them, hydrogen bonds are particularly attractive because they dominate many important structures and functions in nature from elegant base-pair interactions in DNAs to sophisticated protein folding and are regarded as an important element in the discovery of new pharmaceuticals. To better elucidate fundamental mechanisms, many studies have been carried out by using conventional spectroscopic methods where the signals stem from the ensemble experiments and the hydrogen-bond dynamics were deduced indirectly. Direct observation of the dynamic process of hydrogen bonds at the single-molecule level, is important, however more difficult.

To tackle the challenge, recently an elegant collaboration of Prof. Guo's group at Peking University, China, Yang's group at University of Science and Technology of China, and Zhong's group at the Institute of Chemistry, China [1] demonstrated direct electrical measurements of hydrogen-bond dynamics at the single-molecule/single-event level on the basis of the platform of molecular nanocircuits (Figure 1). A quadrupolar hydrogen-bonding system based on ureido pyrimidine-dione (UPy) was covalently incorporated into two graphene point contacts to build stable hydrogen-bond-bridged single-molecule junctions (HBB-SMJs). The stochastic rearrangement of the hydrogen-bond structure changes the electron transport property of the molecular junction, so the team could follow the hydrogen-bond dynamic process by monitoring the current signal from the HBB-SMJs. The strong donor-donor-acceptor-acceptor (DDAA) array of intermolecular quadruple hydrogen bonding behaves as a good conducting channel and sensing element with superior sensitivity and recognition capability, which is prerequisite for realizing long-term real-time monitoring of the hydrogen-bond dynamic behavior.

On the basis of platform of the designed molecular nanocircuits, the team succeeded in directly observing the current fluctuations, including profound information of hydrogen-bond dynamics with a strong solvent and temperature dependence. To identify the origin of the observed solvent- and temperature-dependent responses in the molecular electronic structure, clear statistic and simulation analysis are performed. Both experimental and theoretical results consistently show that the signals stemmed from the stochastic rearrangement of the hydrogen-bond structure mainly through intermolecular proton transfer and lactam-lactim tautomerism. From the calculated transmission spectra of the possible structures and the relative energies with the statistical results from experiments, the team successfully assigned each current stage to each hydrogen-bond configuration and mapped the whole transformation process.

This article resulted from a close collaboration of chemists, physicists, materials scientists, and engineers and opens up

*Corresponding author (email: xiangdongde@126.com)

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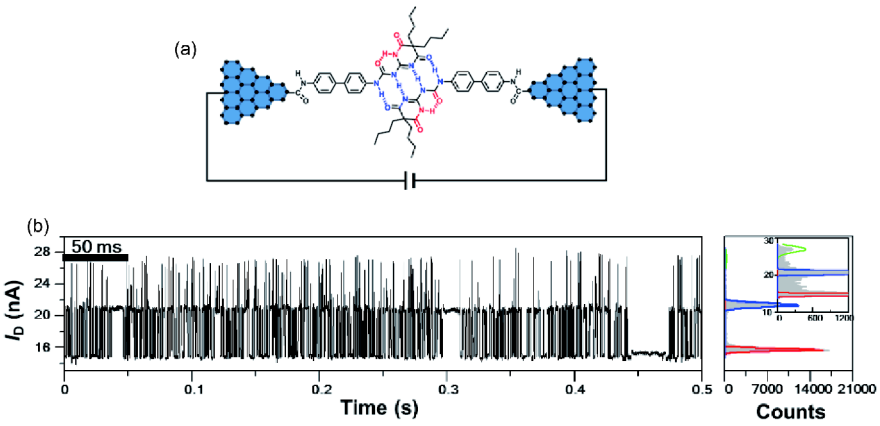

Figure 1 (a) Schematic representation of HBB-SMJs. (b) Typical real-time current recordings of hydrogen-bond dynamics.

unique opportunities to intrinsically transduce the exquisite hydrogen-bond dynamic process into real-time electrical signals at the single-event level and single-bond resolution, making an important contribution to broad fields beyond supramolecular chemistry. With obvious advantages, such as simple fabrication, low cost, no fluorescent labeling/bleaching problems, this single-molecule electronic technique might open a novel and invaluable approach to probe the fundamental molecular mechanisms of chemical reactions and biological activities that are not accessible in conventional ensemble experiments [2].

Conflict of interest The authors declare that they have no conflict of interest.

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2 Xiang D, Wang X, Jia C, Lee T, Guo X. *Chem Rev*, 2016, 116: 4318–4440