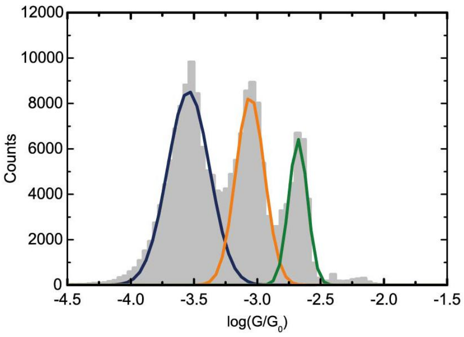
Thermodynamic Study of Single-Molecule Reaction by Electrical Measurement

東工大理[1]　○(M1)張　璐[1]，西野　智昭[1]
Tokyo Institute of Technology[1], °Lu Zhang[1], Tomoaki Nishino[1]
E-mail: zhang.l.aj@m.titech.ac.jp

Electron transport through single molecules receives growing interest to realize the development of functional electronic devices. The metal and the molecular orbital hybridize at the interface, and charge transfer occurs between the metal electrode and the molecule. Besides the device applications, the charge transfer, in which the behaviors of a single molecule are transduced into an electrical signal, allows direct monitoring of a chemical reaction. Such measurements will reveal, e.g., a stochastic nature of the chemical reaction, which cannot be traced with conventional ensemble observations. Several reports have pioneered the observation of the single-molecule reaction based on the electrical measurements. However, discussion from a thermodynamic perspective is still lacking despite its importance to characterize chemical reactions. To address this issue, in the present study, we developed a novel strategy based on electrical single-molecule detection. Specifically, we showed the determination of an equilibrium constant of a single-molecule chemical reaction.

The complexation reaction of DNA with an intercalative dye, ethidium bromide (EB), was studied in the present work. The single-molecule conductance of reactants (DNA and EB) and product (the DNA–EB complex) was measured by the break-junction technique based on scanning tunneling microscopy. The sample surface was prepared by immersion of Au(111) substrates in the solution. The single-molecule conductance of DNA and EB was determined to be 2.5×10^{-4} and 6.1×10^{-4} G_0 ($G_0 = 2e^2/h$), respectively. On the other hand, the DNA-EB complex showed the conductance of 2.2×10^{-3} G_0, and the 10-fold increase in the conductance was ascribed to the increased orbital overlap of the π system of the stacked bases in DNA. Next, the single-molecule conductance was measured in the time domain. Three kinds of conductance values, corresponding to DNA, EB and, DNA–EB, were observed for the mixed solution containing DNA and EB (Figure 1a). The concentration of DNA–EB was related to the observation probability of its single-molecule conductance. Consequently, the binding isotherm was obtained by the repeated measurements using different concentrations of EB (Figure 1b). We used the relevant equation to fit the isotherm to successfully determine the association constant of 4.3×10^5 M^{-1}. We believe that the present methodology provides a unique means to explore single-molecule reactions to achieve novel chemical transformations.

(a)



(b)

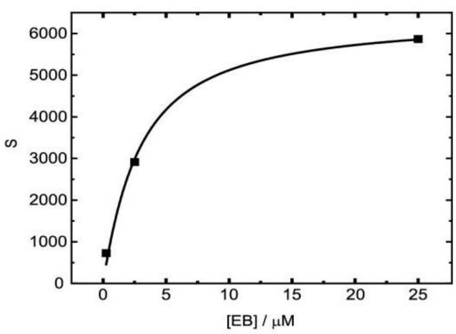


Figure 1. (a) Histogram of single-molecule conductance and (b) binding curve calculated from conductance histogram. The samples were prepared with the mixed solutions of DNA and EB.