

## 論文の内容の要旨

### 論文題目

Electron Microscopic Studies on Dynamics of Organic Molecules  
(電子顕微鏡による有機分子ダイナミクスの研究)

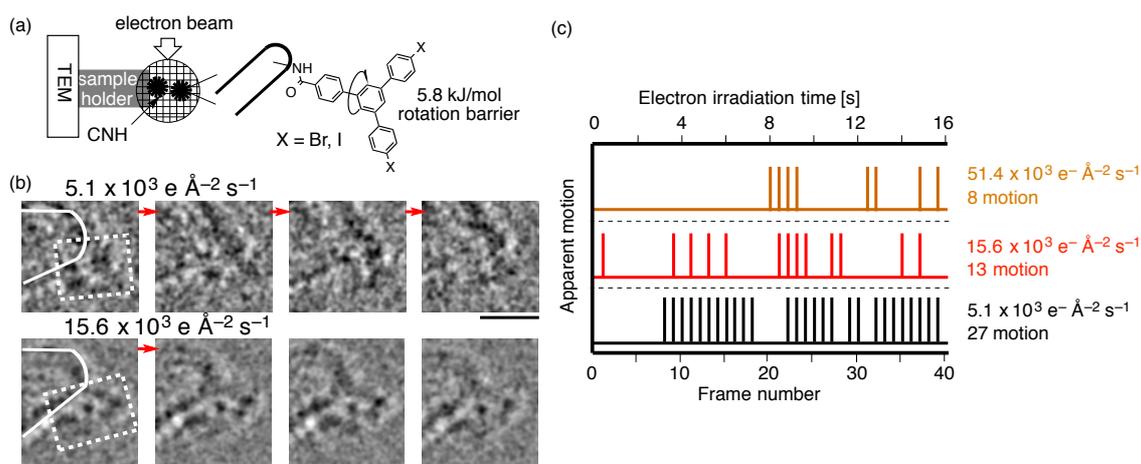
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Any macroscopic chemical events are composed from some number of molecular-level dynamics. However, due to the limitation of methods to visualize single molecules or small molecular clusters, the dynamics of molecules has been studied based on molecular ensembles, such as spectroscopies and optical micrographs. Recent development of electron microscopes gave access to investigate the molecular-level events, but still the observations remained qualitative. In this thesis, I have investigated four systems, namely bond rotation, chemical reaction, crystal nucleation and growth, based on electron microscopic observation and theoretical treatments to demonstrate that the quantitative aspects in the behavior of molecular dynamics.

Chapter 1 describes the short history of investigation of molecular dynamics, namely crystal nucleation, molecular vibration, and chemical reactions. Three approaches are described; theoretical calculations, experimental studies, and microscopic visualization. The achievements and the current issues in electron microscopic imaging are highlighted.

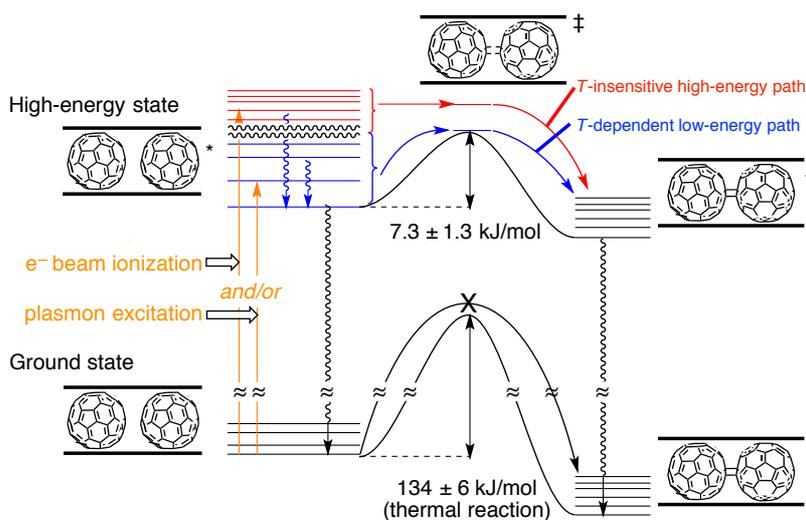
Chapter 2 describes the motion of organic molecules in vacuum and their visualization in single molecule atomic real time transmission electron microscopy (SMART-TEM). A Y-shaped biphenyl rotor attached on a carbon nanohorn has been reported to undergo C-C bond rotation under TEM observation condition as a conformational change between frames (K. Harano *et al. Nat. Mater.* **2012**, 877.). However, the origin of the apparent motion could not be elucidated from the qualitative imaging. I quantitatively analyzed the apparent motion of 4-bromophenyl- and 4-iodophenyl-tagged biphenyl rotor under various electron dose condition.

Based on the TEM images and a quantum mechanical simulation of rotational motion, I found that the each frame of TEM images was constructed from accumulated snapshots of molecules. The observed result that the apparent motion frequencies became small when electron dose rate was increased or substitution with iodine matched with the expectation from the simulation, suggesting the quantum mechanical motion involving in SMART-TEM imaging of organic molecules (Figure 1).



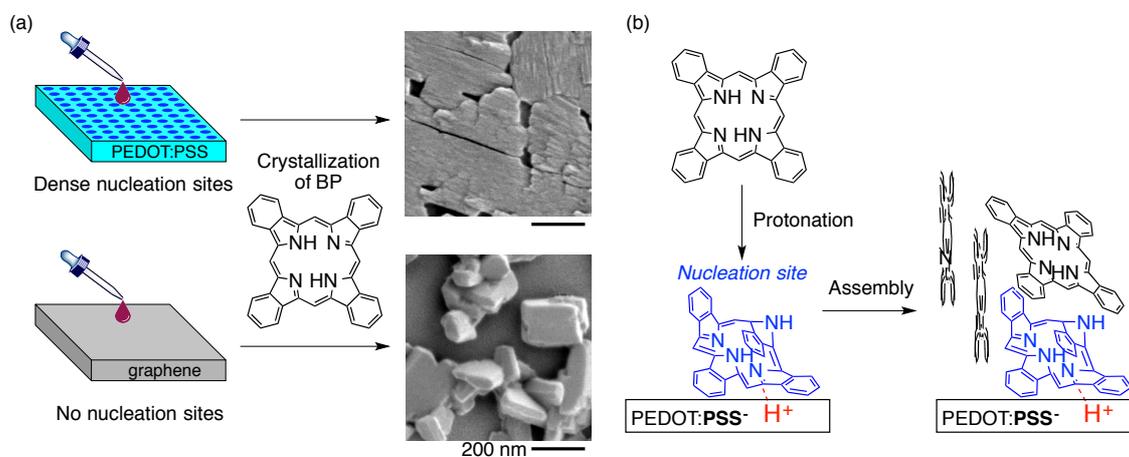
**Figure 1.** Apparent motion of Y-shaped biphenyl rotor. (a) Experimental design. (b) TEM images taken at 120 kV, 293 K at  $5.1$  or  $15.6 \times 10^3$  electrons  $\text{\AA}^{-2} \text{s}^{-1}$ . (c) Appearance of apparent motions during 40 frames.

Chapter 3 describes the dynamics of chemical reactions under SMART-TEM. Previously,  $[2 + 2]$  fullerene dimerization followed by rearrangement to obtain  $C_{120}$  was observed inside carbon nanotube, and their temperature dependence was qualitatively discussed (M. Koshino *et al. Nat. Chem.* **2010**, 117.). Here I analyzed the reaction kinetics based on a Rice-Ramsperger-Kassel- Marcus theory. The observed each reaction event was cumulated and fitted to find that both dimerization and rearrangement processes follow first-order kinetics. This result shows that the kinetic analysis is possible at  $10^{-22}$ -mol scale. The energy barrier for the reactions was elucidated from the fitting of temperature-dependent reaction rate. Both reactions contained two energetically different reaction pathways; temperature-dependent path from triplet excited state, and temperature-insensitive path in which higher energy states (Figure 2).



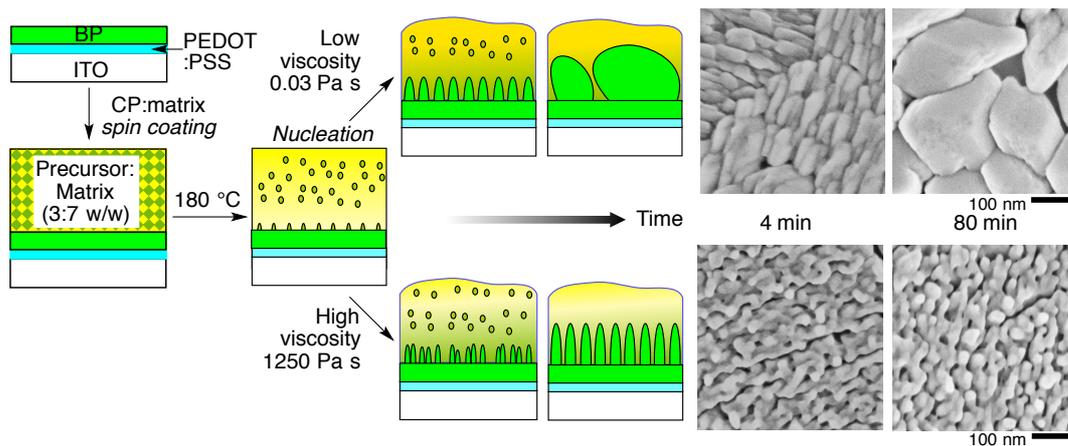
**Figure 2.** An energy diagram of C<sub>60</sub> dimerization.

Chapter 4 describes the mechanism of heterogeneous nucleation of two typical donor molecules for organic solar cells; tetrabenzoporphyrin (BP) and poly(3-hexylthiophene-2,5-diyl) (P3HT). State-of-the-art scanning electron microscopy (SEM) revealed that both BP and P3HT form polycrystalline flat film with the size of several tenth of nanometers on poly(3,4-ethylenedioxythiophene) poly(4-styrenesulfonate) (PEDOT:PSS), a *de facto* standard anode buffer material. On the other hand, they formed randomly dispersed submicron crystals or submicron crystalline domain structure on graphitic surface. From other supporting experiments, the surface acidity of PEDOT:PSS was found to nucleate BP and P3HT by immobilizing one molecules on the surface of PEDOT:PSS (Figure 3).



**Figure 3.** Morphological difference of BP on PEDOT:PSS and HOPG. (a) Schematic images and SEM images. (b) Mechanism of BP nucleation on PEDOT:PSS.

Chapter 5 describes the dynamics of crystal growth of BP controlled by the viscosity of crystallization environment. BP film is prepared on a polycrystalline flat BP film by casting its soluble precursor solution with some organic matrices, and the crystal size of the additional BP layer depends on the viscosity of the matrices at 180 °C, at which temperature BP is generated from the precursor (M. Oiki, *M. S. Thesis*, UTokyo, 2012). I revealed the molecular-level insight into the dependence of the morphology by spectroscopies, analysis of time-dependent morphologies in SEM, and numerical simulation. I found that the crystal growth of BP takes place at the order of seconds in high viscous matrices such as phenyl-C<sub>61</sub>-butyric acid butyl ester, a typically used acceptor molecule (1250 Pa s at 180 °C), that explains the completion of crystallization in four minutes and the negligible increase in size under further heating (Figure 4).



**Figure 4.** Time evolution of the morphologies of BP in matrices with different viscosity.

Finally, Chapter 6 summarizes the present thesis and presents possible outcomes for further study of dynamics of molecules utilizing electron microscopes.