

Substrate-Dependent Interface Structures between Ionic Liquids and Solid Substrates Revealed by Electrochemical FM-AFM

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Microscopic understanding of the local structure of electric double layer at liquid / electrode interfaces are crucial for technological applications such as secondary batteries, fuel cells, dye-sensitized solar cells. Ionic liquids (ILs) are of particular importance for such applications due to their wide electrochemical window, nonflammability, etc. One of successful applications is field-effect transistor using IL for gate electric layers on organic crystals (IL-OFET) such as rubrene [1]. But ILs provide quite unusual double layer structure at the interfaces. Layered structures at the solid interfaces were suggested by experimental and theoretical studies. Recently, we have developed electrochemical frequency-modulation atomic force microscopy (EC-FM-AFM), which can be applicable to analyses of electrochemical systems with an advantage on high spatial resolution at low loading forces [2,3], and applied this method to IL/solid interfaces [4]. In this presentation, we show unexpected substrate-dependent interface structures revealed by FM-AFM observations.

As we already reported [4], solid-like layered structures of IL with a step height

corresponding to the ion-pair diameter (0.79 nm) of BMIM-TFSI are found at the IL/graphite (HOPG) and IL/mica interfaces (Fig. 1(a)). In contrast, quite different images were obtained at the rubrene crystal interface (Fig. 1(b)). The step height coincided to that of rubrene(001) and each rubrene molecule was imaged at the terrace, i.e. no solid-like IL at the interface. Possible origins of different interface structures and dynamic aspects of the structures observed during FM-AFM measurements and by changing electrochemical potential of the substrate electrodes will be discussed.

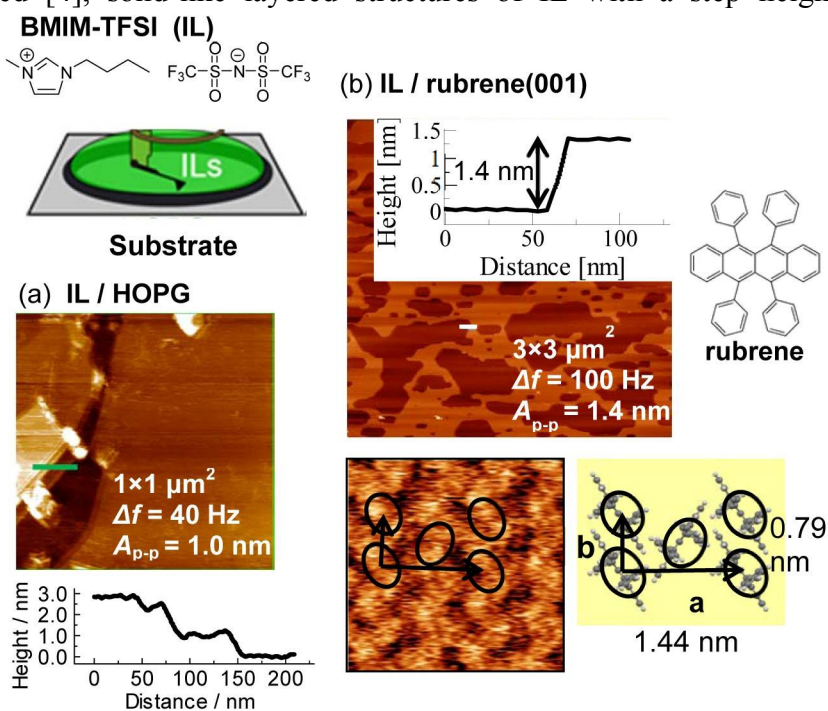


Figure 1 FM-AFM topographic images of BMIM-TFSI / solid substrate interfaces under a few-mm liquid phase. Distinct differences of the interface structure were found between (a) HOPG (or mica) [4] and (b) rubrene (001) substrate.

References

- [1] S. Ono, S. Seki, R. Hirahara, Y. Tominari, J. Takeya, *Appl. Phys. Lett.* **92**, 103313 (2008)
- [2] K. Umeda and K. Fukui, *Langmuir* **26**, 9104 (2010).
- [3] K. Umeda and K. Fukui, *J. Vac. Sci. Technol. B* **28**, C4D40 (2010).
- [4] Y. Yokota, T. Harada, and K. Fukui, *Chem. Commun.* **46**, 8627 (2010).