Electronic Supplementary Information (ESI)

Chemical Liquid Deposition of π-Conjugated Polymers onto Graphite by Spontaneous On-Site Polycondensation in Aqueous Solution

Rintaro Higuchi, Ryota Tanoue, Nobuo Enoki, Shigeyasu Katahira, Yuya Miyasato, Kazuki Sakaguchi, Shinobu Uemura, Nobuo Kimizuka and Masashi Kunitake*
*Department of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan, Fax: (+) 81-96-342-3679; Tel: (+) 81-96-342-3674
E-mail: kunitake@kumamoto-u.ac.jp

Experimental Section

The chemicals used and preparation of the solution is described in our previous paper[1]. HOPG was purchased from Atomgraph AG and was cleaved immediately before immersing into the reaction solution. The concentrations of the ASB and aldehyde monomers (TPA, IPA, PDA, TCA) were typically 0.1 mM. Controlling the pH of the solution was achieved through the addition of dilute HCl and NaOH solution without a buffer. After deposition, the substrates were picked from the solutions, rinsed thoroughly in ultrapure water, and then dried.

The UV-Vis reflection spectra of the polymer films were measured using a UV-Vis spectrophotometer (MCPD 7000, Otsuka Electonics). The surface morphologies were imaged by atomic force microscopy (5500 AFM/SPM, Agilent) using silicon tips (OMCL-AC240TS-C2, Olympus) with a resonance frequency of ca. 70 kHz., and by field emission scanning electron microscope (S-4800, Hitachi) without deposition. The film thicknesses and the influence of reflection angle were measured by ellipsometer (FE-5000S, Otsuka Electronics).

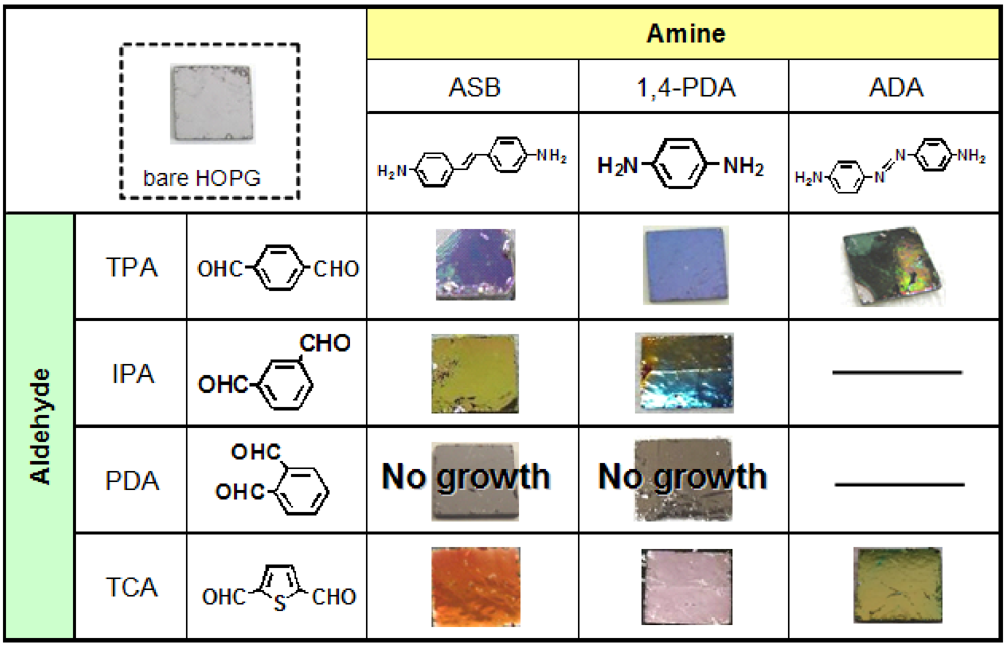


Figure S1. Photographs of polymer films formed on HOPG with different combinations of building blocks.

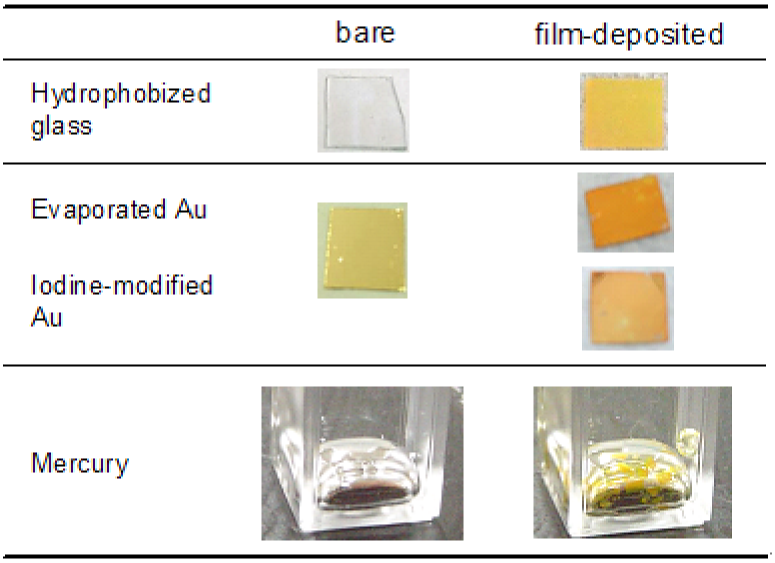


Figure S2. Photographs of the deposited films on each substrates and interface. The conditions of the deposition are similar to the case with a HOPG substrate: pH = 2.7-2.8; and T = 303 K. Hydrophobized grass was prepared by the silane coupling treatment of glass slides with n-octyltriethoxysilane. Evaporated Au was prepared by vapor deposition of Au wire. For iodine-modified Au, 10 mM potassium iodide was added to the monomer solution.

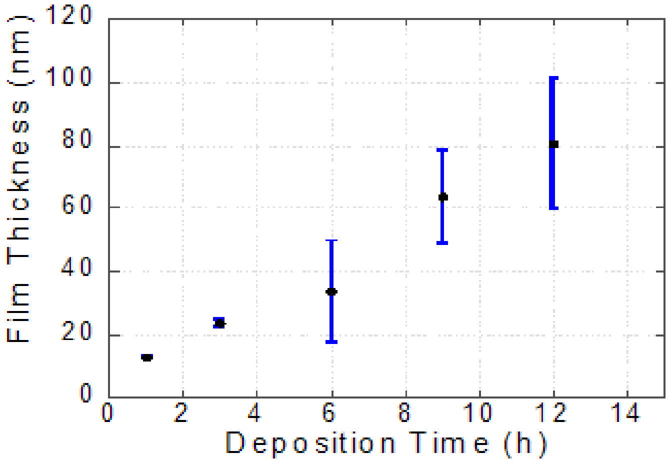


Figure S3. Film thicknesses of ASB-TCA Schiff-base polymer films deposited on HOPG at different deposition times.

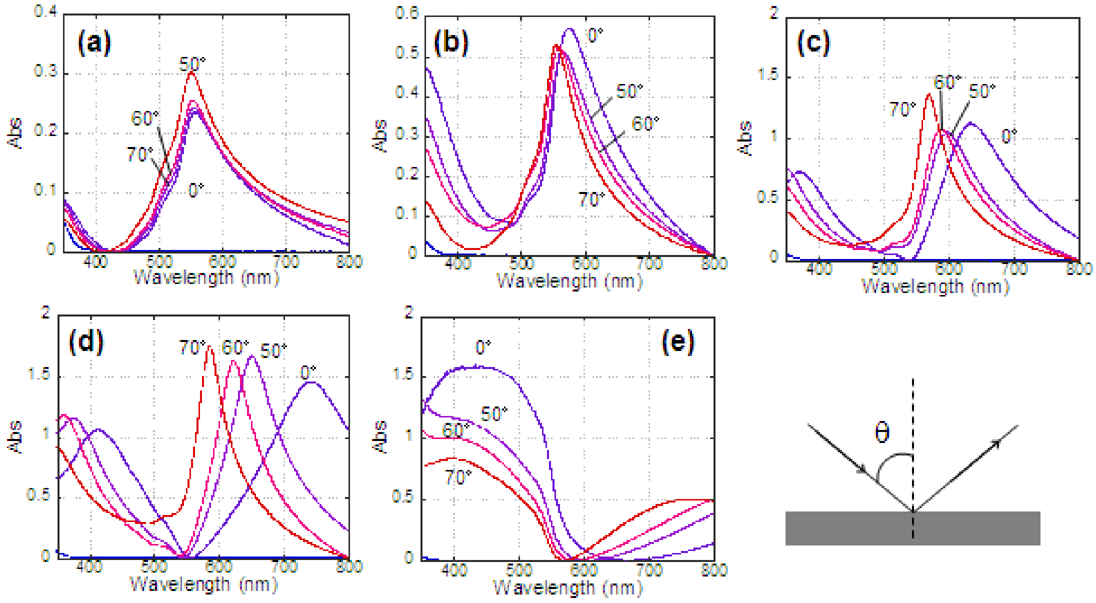


Figure S4. UV-Vis absorption spectra of Schiff-base polymer films deposited by ASB-TCA on HOPG while varying the reflection angle (0-70 degree). The deposition times are: 3, 6, 9, 12 and 24 hours for (a)-(e), respectively.

Because of the angle dependence of the UV-Vis reflection spectra (see Fig. S4), structural color originating from a sponge-like structure influenced the UV-Vis spectra. However, the absorption band energy was predominantly decided by the chemical nature of the film because the influence of deposition time is greater than the angle dependence (see Fig. S4 in ESI).

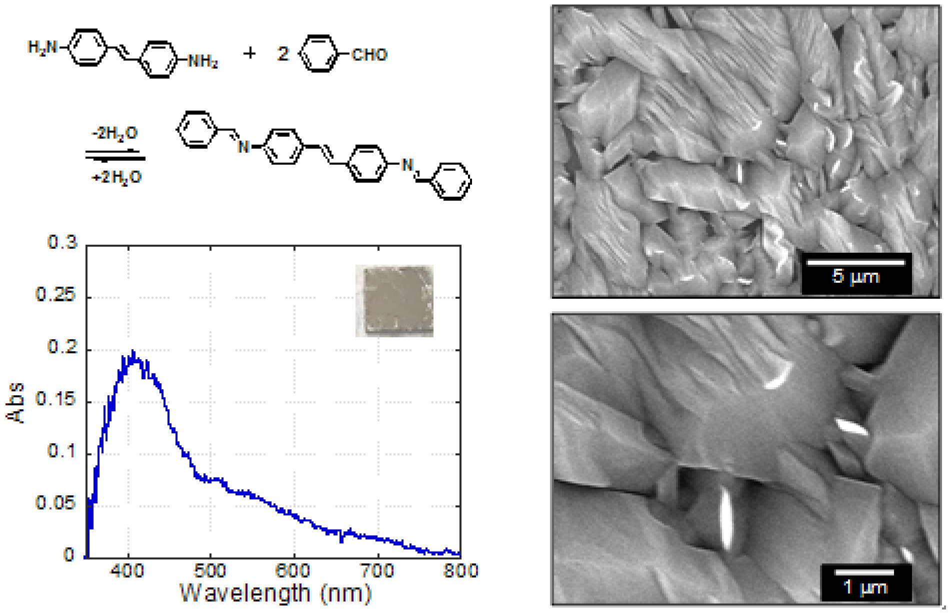


Figure S5. (A) Reflection UV-Vis spectrum and photograph of a monomeric Schiff-base film deposited from the combination of ASB-Benzaldehyde, and (B) SEM images of the film surface. CLD was conducted in an aqueous solution containing 0.5 mM monomers. pH = 2.8; deposition temperature = 303 K; and deposition time = 48 hours.

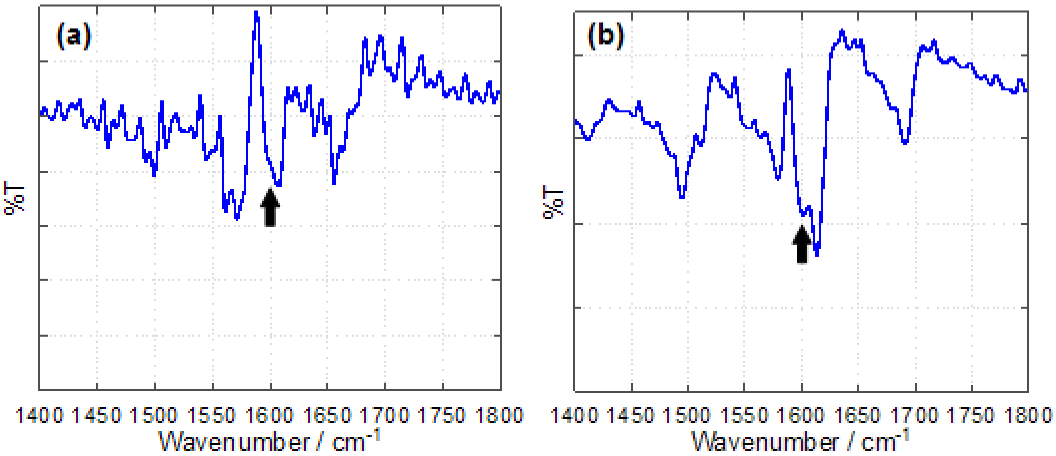


Figure S6. Typical reflection IR spectra of (a) ASB-TCA and (b) ASB-TPA Schiff-base polymer films.

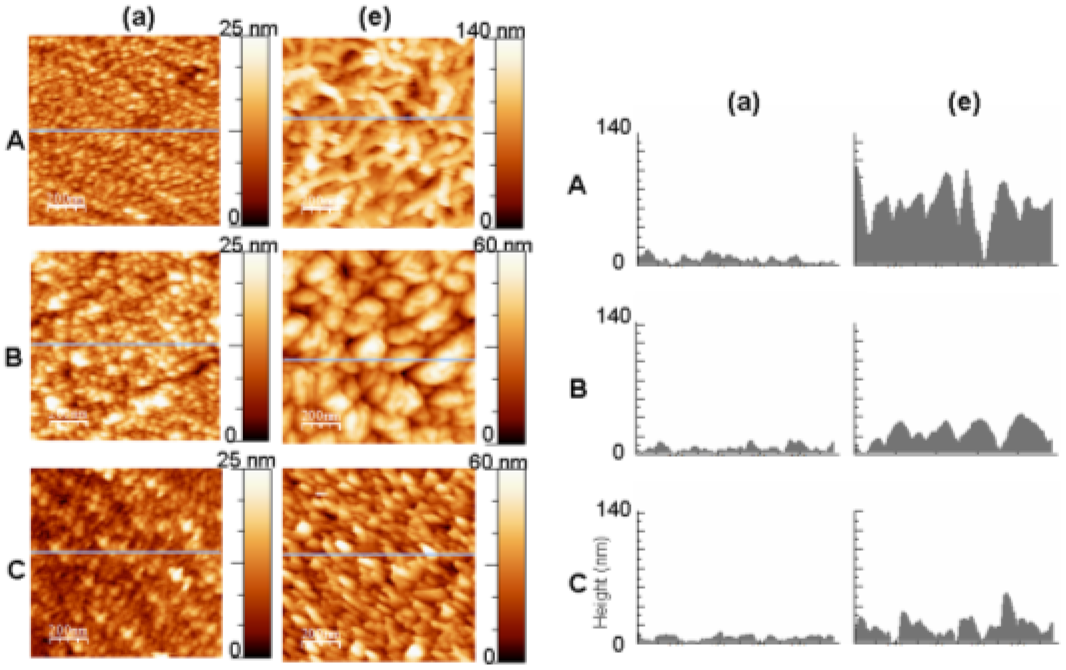


Figure S7. Tapping-mode AFM images and the cross-sectional view of polymer films of (A) ASB-TCA, (B) ASB-TPA, and (C) ASB-PDA. The conditions for CLD are as follows: the deposition time was 3h (a) or 24 h (e); the pH of the solution was 2.8 (A, B) and 4.5 (C); and the depositing temperature was 303 K.

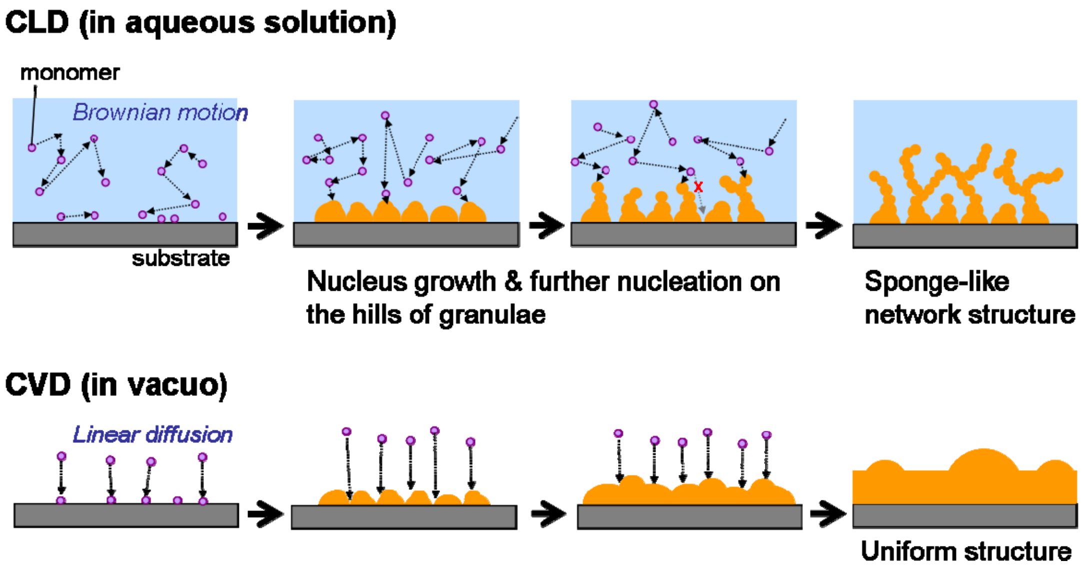
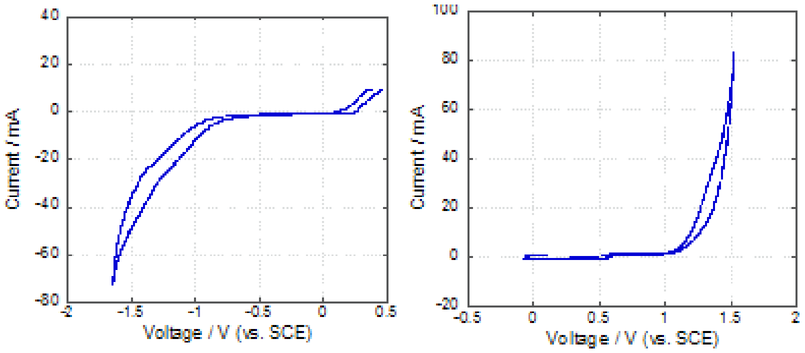


Figure S8. Schematic representation of the comparison of deposition mechanisms based on “random walk" diffusion and linear diffusion for CLD conducted in a solution and Chemical Vapor Deposition (CVD) in vacuum, respectively.



$E_{onset,red}$ / V	$E_{onset,ox}$ / V	LUMO / eV	HOMO / eV	Eg / eV
-0.84	1.14	-3.84	-5.44	1.60

Figure S9. Typical cyclic voltammetry of ASB-TCA Schiff-base polymer film deposited on a HOPG in acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$. Scan rate = 20 mV/s. The potential was normalized by the redox potential of ferrocene which was added in the electrolyte after the measurement. The energy band gap (Eg) was calculated using the onset voltages ($E_{onset, red}$ and $E_{onset, ox}$).[2]

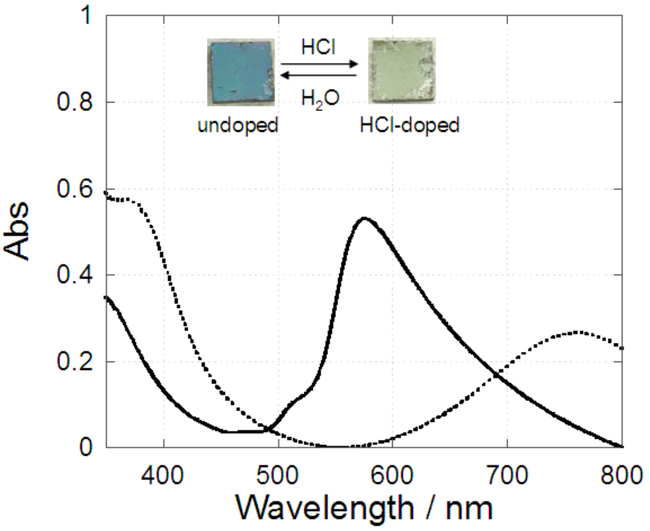


Figure S10. Typical example of post doping of CLD film, UV-Vis absorption spectra and color photo images of undoped (solid line) and HCl-doped (dotted line) states of a ASB-TCA polymer film, which was prepared by the condition; pH 2.8, deposition temperature 303 K, deposition time 6 hours. Post doping with HCl was carried out by exposing the film into HCl fume from 12 N HCl solution.

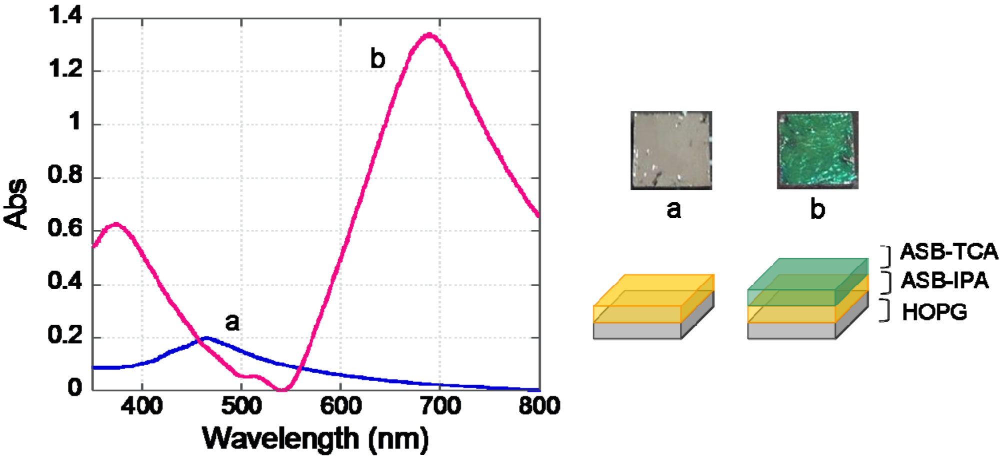


Figure S11. UV-Vis reflection spectrum and photograph of ASB-IPA Schiff-base polymer film deposited on (a) HOPG and (b) ASB-TCA polymer films deposited on a ASB-IPA polymer film as a hetero-film.

References

[1] R. Tanoue, R. Higuchi, N. Enoki, Y. Miyasato, S. Uemura, N. Kimizuka, A. Z. Stieg, J. K. Gimzewski and M. Kunitake, *ACS Nano* 2011, **5**, 3923.

[2] V. P. Barberis, J. A. Mikroyannidis and V. Cimrova, *J. Polym. Sci. Part A: Polym. Chem.* 2006, **44**, 5750.