Highly Organized Phthalocyanine Assembly onto Gold Surface through Spontaneous Polymerization

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Soluble μ-dihydroxysilicon-tetra-*t*-butylphthalocyanine was immobilized onto OH-coated gold surface. The phthalocyanine was immobilized in a sigmoidal manner with two threshold times, and the process was successfully analyzed with QCM and AFM studies. UV–vis studies indicated the highly organized polymer structure deposited onto the surface.

Organizing molecules into supramolecular, polymeric, and crystalline architecture onto a solid surface at the nano- and upward scales is one of the key challenges of supramolecular, polymer, material, and surface science. For electronics, optoelectronics, and nonlinear optics device applications, various quasi-one-dimensional (Q1D) semiconductors, including molecular solids made of π-building blocks and σ/π-conjugating polymers, are of particular importance as candidates due to their effective quantum confinement.[1] Exploring such an ideal self-organization, however, remains an issue due to the lack of proper model supramolecular system and detecting apparatus with ultrahigh sensitivity. This is presumably due to limited knowledge and understanding on the deposition process of the building block at the liquid/solid interface and on the nature of attracting forces between the block and interface.

To elucidate spatio-temporal evolutional organization of a building block into a π-conjugating architecture at the liquid/solid interface in a controlled manner, we chose μ-dihydroxysilicon-tetra-*t*-butylphthalocyanine (ttbPcSi(OH)$_2$, Figure 1a).[2] This served as a model of soluble π-type square planer building blocks with reactive bi-functional OH groups at the center of Pc ring and the OH-coated gold surface treated with 6-hydroxyhexane-1-thiol (HOC6SAu),[2] one of the most useful solid surfaces with a functional OH group. For comparison, free-base tetra-*t*-butylphthalocyanine (ttbPcH$_2$) was used as a model of soluble Pc without reactive functional groups.[2]

The present work demonstrated a combined study of the 9-MHz quartz crystal microbalance (QCM) measurement with atomic force microscopy (AFM) observation and elucidated a rapid self-propagation of ttbPcSi-based nanoarrays onto the OH-coated gold substrate, leading to self-deposition of ttbPcSi-based ultrathin film with high degree of polymerization by UV–vis studies.

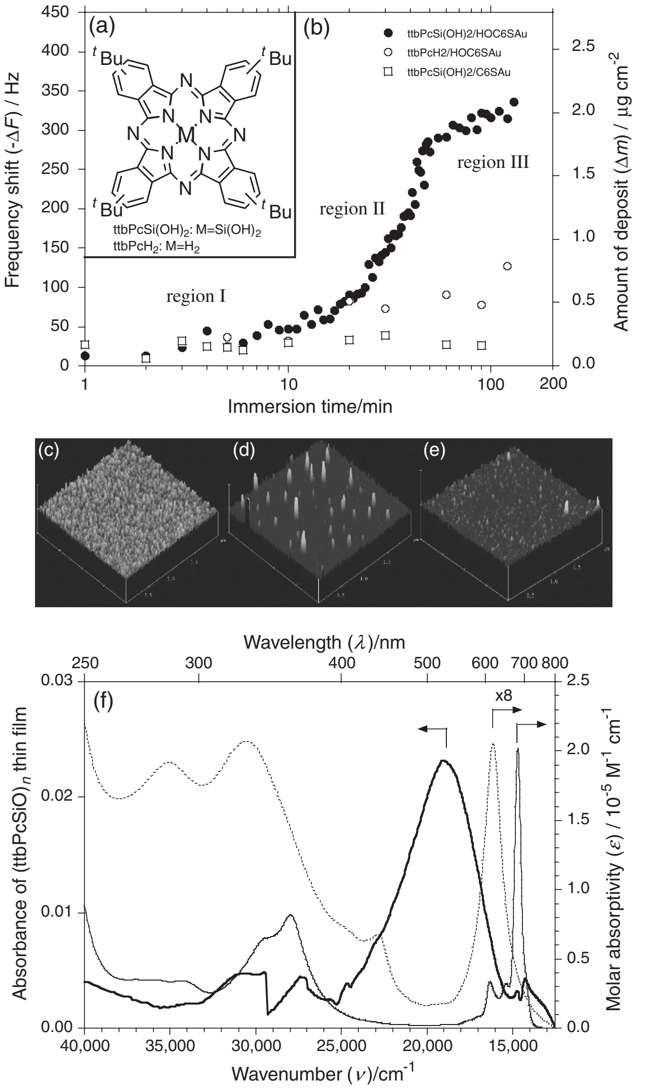

Figure 1. (a) Chemical structure of ttbPc derivatives in this work. (b) The amount of immobilized ttbPcSi(OH)$_2$ and ttbPcH$_2$ on the OH-coated gold surface, and ttbPcSi(OH)$_2$ on the alkane-coated gold surface by QCM method under 1.5×10^{-5} M chloroform solution. Typical AFM images of the deposited thin film. [(c) 1 min, (d) 10 min, (e) 120 min; Area: 2 × 2 μm, Height: 10 nm] (f) UV–vis spectra of the deposited thin film (thick solid line), ttbPcSi(OH)$_2$ (thin solid line), and oligo-(ttbPcSiO)$_n$ (thin dotted line) in CHCl$_3$.

The amount of the adsorbed ttbPcSi(OH)$_2$ on the electrode increased in a sigmoidal manner with two threshold immersion times at 10 and 90 min, as shown in Figure 1b. On the other hand, ttbPcSi(OH)$_2$ on *n*-alkane-coated QCM gold electrode treated with hexane-1-thiol (C6SAu)[2] showed a very weak adsorption even with a prolonged immersion time. Interestingly, even ttbPcH$_2$ was adsorbed on the OH-coated gold surface by one third compared to the corresponding ttbPcSi(OH)$_2$ at a prolonged immersion time. These results led to the idea that ttbPcSi(OH)$_2$ spontaneously adsorbed on the OH-coated gold, probably due to attractive cooperative tandem interactions:[3] (i) OH/π interaction, (ii) OH/HO interaction, (iii) OH/N interaction, (iv) π/π interaction, and (v) CH/π interaction. It is therefore assumed that ttbPcH$_2$ spontaneously deposited on the OH-coated gold by OH/π, OH/N, π/π, and CH/π interactions between the OH-coated gold and ttbPc.

To further clarify the adsorption mechanism and deposition kinetics of ttbPcSi(OH)$_2$ on the OH-coated gold, the change in mass were classified into three regions I (0–10 min), II (10–90 min), and III (90–120 min), as shown in Figure 1b. Although ttbPcSi(OH)$_2$ in the region I gradually deposited on the gold, ttbPcSi(OH)$_2$ in the region II steeply deposited exceeding the 10 min-threshold, and the region III was a plateau region with a constant value.

The Avrami equation,[4] $\theta(t) = 1 - \exp(-K{\cdot}t^n)$, was successfully applicable to analyze the apparent sigmoidal behavior,[2] where θ is the weight fraction of ttbPcSi(OH)$_2$ deposited onto the substrate with immersion time t at room temperature relative to a maximum frequency shift, $\Delta F_{\max}$, at the prolonged immersion of ca. 120 min, K a temperature-dependent constant, n Avrami index depending on nucleation and propagation manners of ttbPcSi(OH)$_2$, although this equation was originally formulated to characterize isothermal nucleation and crystallization kinetic of polymers. The value of $\Delta F_{\max}$ in this study was chosen as 350 Hz, which is responsible for a maximum deposit value ttbPcSi thin solid film. Although the evaluated n value of ca. 0.7 in the region I infers an inhomogeneous nucleation, the n value ca. 1.5 in the region II is an intermediate between Q1D and Q2D self-organizations of ttbPcSi(OH)$_2$ stacks. The total amount of ttbPcSi(OH)$_2$ at the equilibrium region III led to the idea that 2.2 μg·cm^{-2} of ttbPcSi(OH)$_2$ molecules, corresponding to ca. 50 nm or ca. 150 Pc repeating units in length,[5] self-organized into the corresponding ttbPcSi assembly.

To assess the validity of direct immobilization and spontaneous deposition of soluble ttbPcSi(OH)$_2$, AFM images at three regions I, II, and III were obtained. Although 1-min immersion in the region I process provided ttbPcSi(OH)$_2$ domains (Height: 0.3–3 nm) aligned with side-by-side organization (Figure 1c), the domains immediately disappeared, and a 10-min immersion procedure then induced an abrupt appearance of small nucleus domains spread throughout the observing area (Figure 1d). The domain areas then vertically grew as needle-like nanoarchitecture after further immersion time. These snapshots could be consistent with the inhomogeneous nucleation of Q1D- and Q2D-propagation kinetics from the surface based on the Avrami plot. A prolonged immersion for 120 min eventually led to an almost uniform ultrathin film based on ttbPcSi(OH)$_2$ with minimal defects (Figure 1e).

All UV–vis absorption spectra of the thin film onto the OH-coated gold-on-sapphire[3] and chloroform solution (5.0×10^{-6} M) of ttbPcSi(OH)$_2$ and chemically synthesized oligo-(ttbPcSiO)$_n$[2] are displayed in Figure 1f. The thin film which had a very broad Q-band at 19120 cm^{-1} (523 nm), was greatly blue-shifted by 4436 cm^{-1} with fwhm of ca. 5000 cm^{-1}, compared to that of the corresponding monomeric ttbPcSi(OH)$_2$. Compared to the Q-band of ttbPcSi(OH)$_2$ (14684 cm^{-1}, 681 nm), the Q-band of oligo-(ttbPcSiO)$_n$ with ca. 18mer (16129 cm^{-1} with fwhm of ca. 1350 cm^{-1}, $\lambda_{\max} = 620$ nm) was blue-shifted by 1445 cm^{-1} ($\Delta\lambda_{\max} \approx 61$ nm). This means that the Q-band of the thin film was further blue-shifted by 2991 cm^{-1} ($\Delta\lambda_{\max} \approx 97$ nm), when compared to that of the oligo-(ttbPcSiO)$_n$, suggesting a greater DP of the deposited ttbPcSi with the H-type assembly. In addition, formation of Si–O–Si bonding in the backbone was confirmed by IR signal band at 1013 cm^{-1}, assigned to ν_{as} (Si–O–Si). This idea was supported from an estimated molecular image height of ca. 50 nm (ca. 150 Pc) for the deposited ttbPcSi nanoarrays measured by QCM analysis, as shown in Figure 1b.

In conclusion, this letter first characterized organization of soluble ttbPcSi(OH)$_2$ bearing two reacting Si–OH groups at the chloroform/OH-coated gold interface by means of QCM, AFM, and UV–vis experiments. Self-immobilization (Avrami index, $n \approx 0.7$) and self-polymerization (Avrami index, $n \approx 1.5$) of ttbPcSi(OH)$_2$ were successfully analyzed by the Avrami equation from time-course QCM experiment. AFM study proved the spatio-temporal organization of ttbPcSi-based nanoarrays at the interface, leading to an almost uniform ultrathin film. The present built-up approach may be regarded as a programmed switching from a supramolecular approach to hierarchical polymer organizations.

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