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Description	

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Metal-Organic Coordination Network Thin Film by Surface-Induced Assembly

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KEYWORDS: Porphyrin, Self-assembly, Multilayer thin film, Surface-Induced Assembly (SIA), Organized structure

ABSTRACT

The growth of metal-organic coordination network thin films on surfaces has been pursued extensively and intensively to manipulate the molecular arrangement. For this study, the oriented multilayer thin films based on porphyrinic nano-architecture were synthesized toward metal-organic coordination networks using surface-induced assembly (SIA). Nanoscale molecular thin films were prepared at room temperature using cobalt(II) ion and porphyrin building blocks as precursors. Stepwise growth with a highly uniform layer was characterized using UV-Vis, AFM, IR, and XPS studies. The grazing incidence small angle X-ray scattering (GI-SAXS) and X-ray reflectivity (XRR) results remarkably suggested a periodic structure in in-plane (IP) direction with constant and high mass density (ca. 1.5 g/cm^3) throughout the multilayer formation. We propose that orientation of the porphyrin macrocycle plane with a hexagonal packed model by single anchoring mode was tilted approximately 60° with respect to the surface substrate. It is noteworthy that the well-organized structure of porphyrin-based macrocyclic framework on the amine-terminated surface substrate can be achieved efficiently using a simple SIA approach under mild synthetic conditions. The synthesized thin film provides a different structure from that obtained using bulk synthesis. This result suggests that the SIA technique can control not only the film thickness, but also the structural arrangement on the surface. This report of our research provides insight into the ordered porphyrin-based metal-organic coordination network thin films, which opens up opportunities for exploration of unique thin film materials for diverse applications.

1. INTRODUCTION

Nanostructural materials have been developed continuously because of their higher efficiency than that of conventional materials.[1] The engineering of nanomaterials onto the surface is promoted more progressively via the concept of coordination chemistry and surface science.[2] However, the control of structural arrangement at a nanoscale level is a crucially important and highly challenging aspect of these materials.

Metal-Organic Frameworks (MOFs)[3, 4] are hybrid porous materials composed of a metal cluster connecting with organic linkers. The potential of MOFs is exploited in widely diverse applications including gas adsorption and separation, sensing, optoelectronic, biomedical and catalysis.[5] Thin film assembly techniques for MOFs are necessary to apply to various devices with these applications. The fabrication of MOF thin films on the surface is described using various methods including Layer-by-Layer (LbL) (also Liquid Phase Epitaxy, LPE)[6], Langmuir-Blodgett (LB), microwave, colloidal, electrochemical deposition, inkjet, spray coating[5] and spin coating.[7] Among these methods, LbL is a widely used solution-based fabrication process for control of the generation of the multilayer nanostructure on a surface substrate.[8, 9] Wöll, Fischer and co-workers introduced the LbL method to generate MOF films on surface.[10, 11] The particular MOF thin films in multilayer fashion with nanometer range are recently referred to surface-attached Metal-Organic Frameworks (SURMOFs). The SURMOFs are particularly beneficial because of their highly oriented structure, homogeneous morphology with a smooth surface, precisely controllable thickness via deposition cycle, and less defective framework than bulk synthesis.[12]

Porphyrin is a fascinating candidate for use as a linker backbone in molecular networks. The various functional properties of porphyrin-based materials have been reported, including photosensitizing, optoelectronic, magnetic, molecular recognition, selective gas sorption, and catalytic properties.[13, 14] Numerous bulk porphyrin-based MOFs have been studied, while the

thin films have been less explored.[15] Recently, porphyrin-based MOFs thin films on substrate have been more investigated by Kitagawa and Hupp groups.[16, 17]

Molecular ordering and the alignment direction in the thin film play significant role for the material performance. For example, the edge-on orientation of molecular binding on the surface is preferred for FET devices, whereas the face-on orientation is desirable for photovoltaic devices such as solar cells. Consequently, the determination of molecular alignment is necessary to clarify the appropriate application. The strategy to control the architectures is extremely important. At this point, Surface-Induced Assembly (SIA) is considered for this achievement. Sequential immobilization between metal ion and organic building units on the surface can promote variation of the coordination network structures in a controllable manner. This stepwise growth phenomenon is dissimilar to that of bulk, for which the coordination is simultaneously driven. From this aspect, novel structures on the surface can be discovered using this approach. Synergistic concern between the structural arrangement and the material properties presents a challenging issue for breakthrough in the required utilizations.

In this work, we demonstrated that sequential coordination from a surface substrate creates a new molecular assembly structure. The structure differs greatly from bulk system. We fabricated metal-organic coordination network multilayer from metal ions (Co^{2+}) and deprotonated free-base porphyrin (H_2TCPP^{4-}) using the sequential coordination from the amine-modified surface substrate. Systematic characterization of the multilayered film using optical spectroscopy and X-ray photoelectron spectroscopy (XPS) revealed ideally sequential growth of the coordination network structure. Moreover, the coordination network structure of the multilayered film produced by sequential surface growth was characterized using X-ray scattering. It was completely dissimilar to the bulk structure obtained from conventional synthesis.

2. EXPERIMENTAL

2.1 Materials

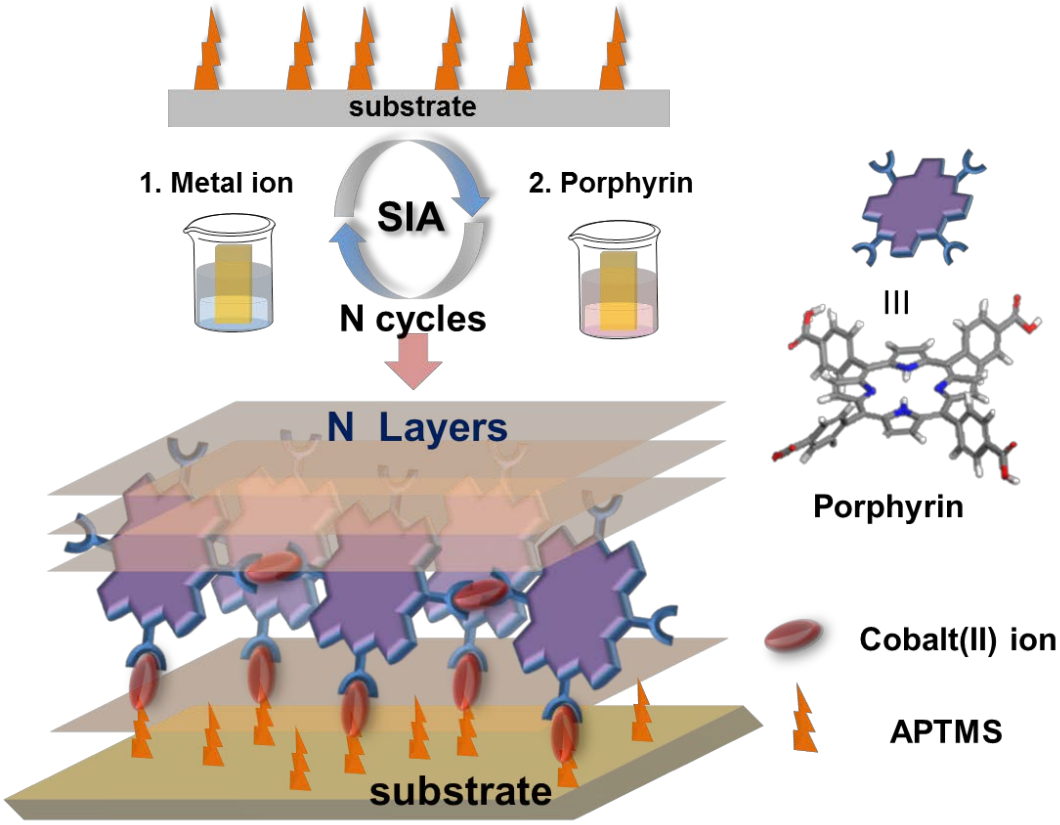
Silicon wafer (100, p-type) substrates were purchased from Electronics and Materials Corp. Ltd. Quartz substrates were purchased from Sendai Sekiei Glass Seisakusho Y.K.. Both substrates were used for SIA deposition. 3-Aminopropyltrimethoxysilane (APTMS, >96%) was purchased from Tokyo Chemical Industry Co. Ltd. (TCI). 5,10,15,20-Tetrakis(4-carboxyphenyl)-porphyrin (H_2TCPP) (purity 98%) was purchased from Strem Chemical Inc., USA. Cobalt(II) acetate tetrahydrate ($Co(OAc)_2.4H_2O$) was purchased from Wako Pure Chemical Industries Ltd. HPLC and AR grade of 2-propanol and ethanol were used for surface modification. Chloroform ($CHCl_3$), methanol and 2-propanol as super dehydrated solvents (low water content; (≤ 0.001% or 10 ppm)) were used with a syringe to prepare solutions for SIA deposition. All solvents were purchased from Wako Pure Chemical Industries Ltd. All chemicals were used as received without further purification.

2.2 Modification of Surface Substrate with Silane Coupling Agent (APTMS)

Before use, silicon wafer substrates (40×25 mm^2) and quartz plate substrates (25×15 mm^2) were cleaned using 2-propanol two times with sonication for 10 minutes. Then they were dried immediately and kept on a clean bench. To obtain the amine-functionalized substrates, all cleaned substrates were immersed in 10 mM ethanol solution of 3-aminopropyltrimethoxysilane (APTMS) at room temperature for 1 hour under argon atmosphere with mild shaking. Then, all substrates were washed respectively with ethanol (2 times), 2-propanol (2 times), and dried. All APTMS-modified substrates were kept in argon atmosphere until use.

2.3 Fabrication of Multilayer Porphyrin-based Coordination Networks on Amine-Functionalized Substrate

To fabricate the multilayer porphyrin-based coordination networks on modified substrates, the SIA method was used via an LbL automated machine. The APTMS-modified substrates were used for all SIA experiments with the following procedures under argon atmosphere: (i) the modified substrates were immersed into 10 mM $Co(OAc)_2.4H_2O$ in the mixture solvent of super dehydrated methanol and chloroform (1:9, v/v) for 10 minutes and were then rinsed with four separated containers of the same ratio mixture solvent as those described above for each 1 minute washing to remove leftover reactants from the surface and were dried by blowing. (ii) then, the metal-terminated substrates were immersed into 0.11 mM H_2TCPP in 2-propanol for 10 minute following the same washing procedure in 2-propanol. The first layer of coordination networks has been generated. The further growth of the multilayer was controlled by repeating the above procedure (Scheme 1). The desired number of layers according to the alternate deposition of metal ion (Co(II)) and organic linker (H_2TCPP) solution is shown as the "N" layers, denoted as $(Co/\ H_2TCPP)_N$.



Scheme 1. Schematic representation of the surface-induced assembly (SIA) process to fabricate porphyrin-based metal-organic coordination network thin films

2.4 Characterization Techniques

UV-Visible absorption spectra of the multilayer film on quartz substrates were measured as a function of number of layers in absorption mode using a spectrophotometer (V-630; Jasco Corp.) at room temperature. The APTMS-modified quartz was used as a background to subtract from each spectrum.

X-ray reflectivity (XRR) was use to ascertain the film thickness, roughness and mass density of the thin film using a high-resolution X-ray diffractometer (ATX-G; Rigaku Corp.). The diffractometer was equipped with a Cu Kα radiation source (λ= 0.1542 nm). The X-rays were generated from a Cu rotating anode (50 kV, 300 mA). The reflective oscillation spectra from the experiment were fitted using software (GXRR; Rigaku Corp.). The fitting curve

was varied from 0.2° to 3°. The difference of the fringe between SAM layer (APTMS) and Si wafer could not be observed (Figure S5). Essentially, the thickness of the SAM layer had little effect on the overall thickness of thin films. Therefore, the thickness of APTMS and thin film has been estimated as a single layer model.

An atomic force microscope (AFM) with tapping mode was utilized to investigate the surface morphology and roughness of thin film. AFM images were collected using a digital AFM system (Nanoscope IIIa; Veeco Instruments). Silicon cantilevers (SI-DF3FM; Nanosensors Corp.) with a spring constant between 2.8 N/m and 4.4 N/m and a resonance frequency of 79-89 kHz were used. The measurement was proceeded under air atmosphere with a scan rate of 0.4 Hz and scanned area of 1×1 μm^2.

The thickness measurement was conducted using AFM (VN-8000; Keyence Co.) with DFM/SS mode cantilever (OP-75041; Keyence Co.). Prior to measurement, the thin film on Si wafer substrate was removed by sharp blaze without damaging the hard substrate surface. The analysis was done across the scratched line in at least five different positions to estimate the average film thickness.

Fourier-transform infrared attenuated total reflectance (FTIR-ATR) was handled to obtain the molecular vibration of chemical bond in chemical precursors and the bulk sample. The IR spectrum was acquired using an FT-IR spectrometer (Nicolet 6700; Thermo-Fisher Scientific) equipped with a deuterated triglycine sulfate (DTGS) detector. All spectra were recorded with 64 scans and 4 cm^{-1} resolution. Infrared p-polarized multiple angle incidence resolution spectroscopy (p-MAIRS)[18, 19] was used to clarify the molecular vibration of chemical bond in both of in-plane (2×IP) and out-of-plane (OP) orientation of thin film sample. The p-MAIRS measurements were conducted on a FT-IR spectrometer (Nicolet 6700; Thermo-Fisher Scientific) equipped with a mercury-cadmium-telluride (MCT) detector. Single-beam spectra were collected from 38° to 8° by means of 6° steps in a range of angle of

incidence with 64 scans and 4 cm^{-1} resolution. The aperture was fully opened (size of 150). A metal plate with small pores was placed in the light path of the incident beam to prevent saturation. A ZnSe polarizer was used to obtain the p-polarized light. The APTMS-modified silicon wafer substrate was used as a background in p-MAIRS measurement. All p-MAIRS measurements were done under N_2 atmosphere at room temperature.

X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition of thin film on Si wafer and bulk sample on carbon tape. The XPS experiment was conducted using a spectrometer (Axis-Ultra DLD; Kratos Analytical Ltd.) with an Al Kα radiation source (1486.6 eV). The binding energies were calibrated using C1s peak at 284.5 eV as a standard. Curve fitting was performed by processing software (Vision) using a Gaussian envelope with Shirley background correction.

Powder X-ray diffraction (PXRD) was used to investigate the crystalline properties of a synthesized bulk sample. Measurement was carried using a high-resolution X-ray diffractometer (ATX-G; Rigaku Corp.) equipped with a Cu Kα radiation source (λ= 0.1542 nm.) at the step size of 0.02°.

Grazing incidence small angle X-ray scattering (GI-SAXS) measurement was performed to observe the thin film interior structure. Measurement was taken using X-ray diffractometer (FR-E; Rigaku Corp.) with two-dimensional (2D) detector (R-AXIS IV; Rigaku Corp.). The sample stage included the goniometer and a vertical stage (ATS-C316-EM/ALV-300-HM; Chuo Precision Industrial Co. Ltd.). The Cu Kα radiation source (λ= 0.1542 nm.) with beam size of approx. 300 μm × 300 μm and camera length of 300 mm was used. The angle of incidence was varied from 0.21° to 0.22°. The diffraction patterns of in-plane and out-of-plane directions were obtained.

3. RESULTS AND DISCUSSION

3.1 Investigation of Step-by-Step Multilayer Growth

Porphyrinic compounds exhibit characteristic absorption in the UV-Vis region as known as soret band (B-band) and Q-bands, which are useful to follow the multilayer growth of thin film using UV-Vis spectroscopy.[20] The UV-Vis absorption spectra on the transparent quartz substrate displayed the typical intense soret band at 418 nm along with four weak Q-bands at 500-700 nm (Figure 1a). The absorbance increased linearly with the number of deposited layers, which was ascribed to the sequential growth of the multilayer film[20] (Figure 1b). Figure 2 shows the film thickness by XRR and AFM measurements along with the layer growth.[21, 22] Both results are well consistent. Thickness exhibited a linear increase with layer growth. The average thickness per layer was ca.1 nm. Figure 3 shows that the topological thin film exhibited smooth and homogeneous morphology. These results demonstrate to the advantage of the controllable film growth by SIA.

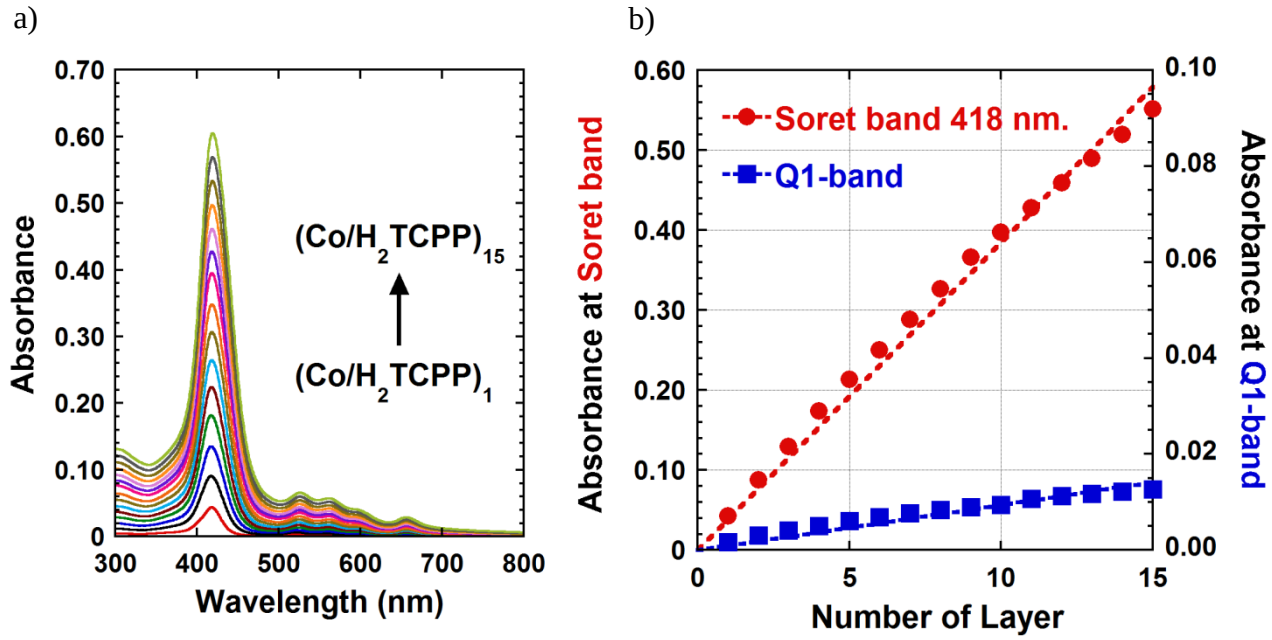


Figure 1. (a) UV-Vis absorption spectra of multilayer thin films as a number of deposited layers $(Co/H_2TCPP)_{1\text{-}15}$ on the APTMS-modified transparent quartz substrate. (b) The UV-

Vis absorption intensity of the soret band at 418 nm and Q_1-band at 526 nm as a number of deposited layers.

a) b)

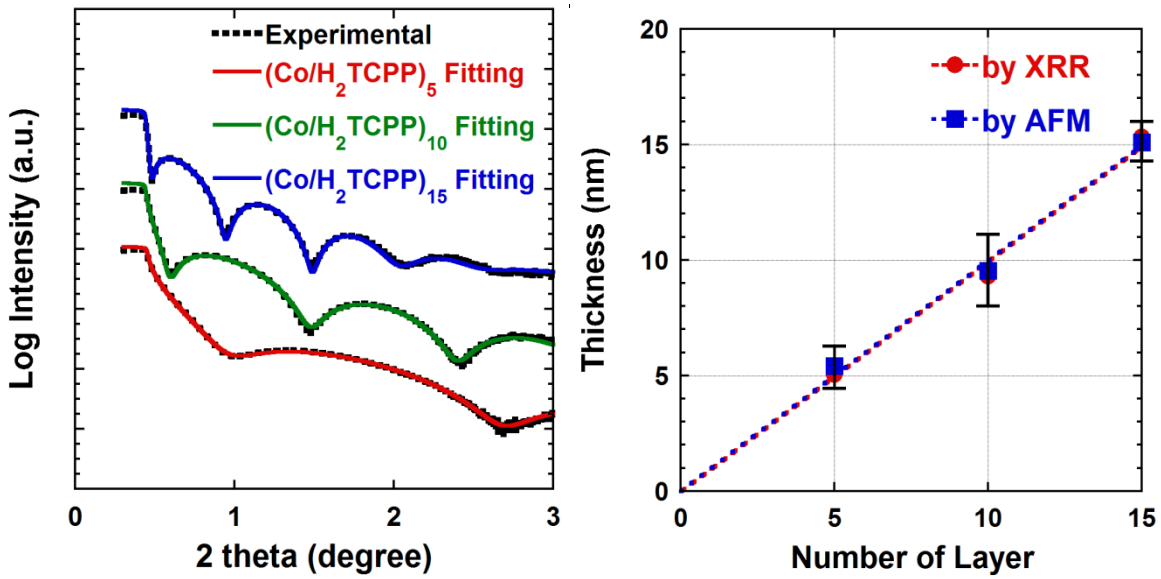


Figure 2. (a) XRR profiles of multilayer films $(Co/H_2TCPP)_5$, $(Co/H_2TCPP)_{10}$, and $(Co/H_2TCPP)_{15}$ on the APTMS-modified Si-wafer substrates. Experimental and fitted data are shown respectively as dashed line and solid line. (b) Thickness of multilayer film comparing between XRR and AFM study with the error bar.

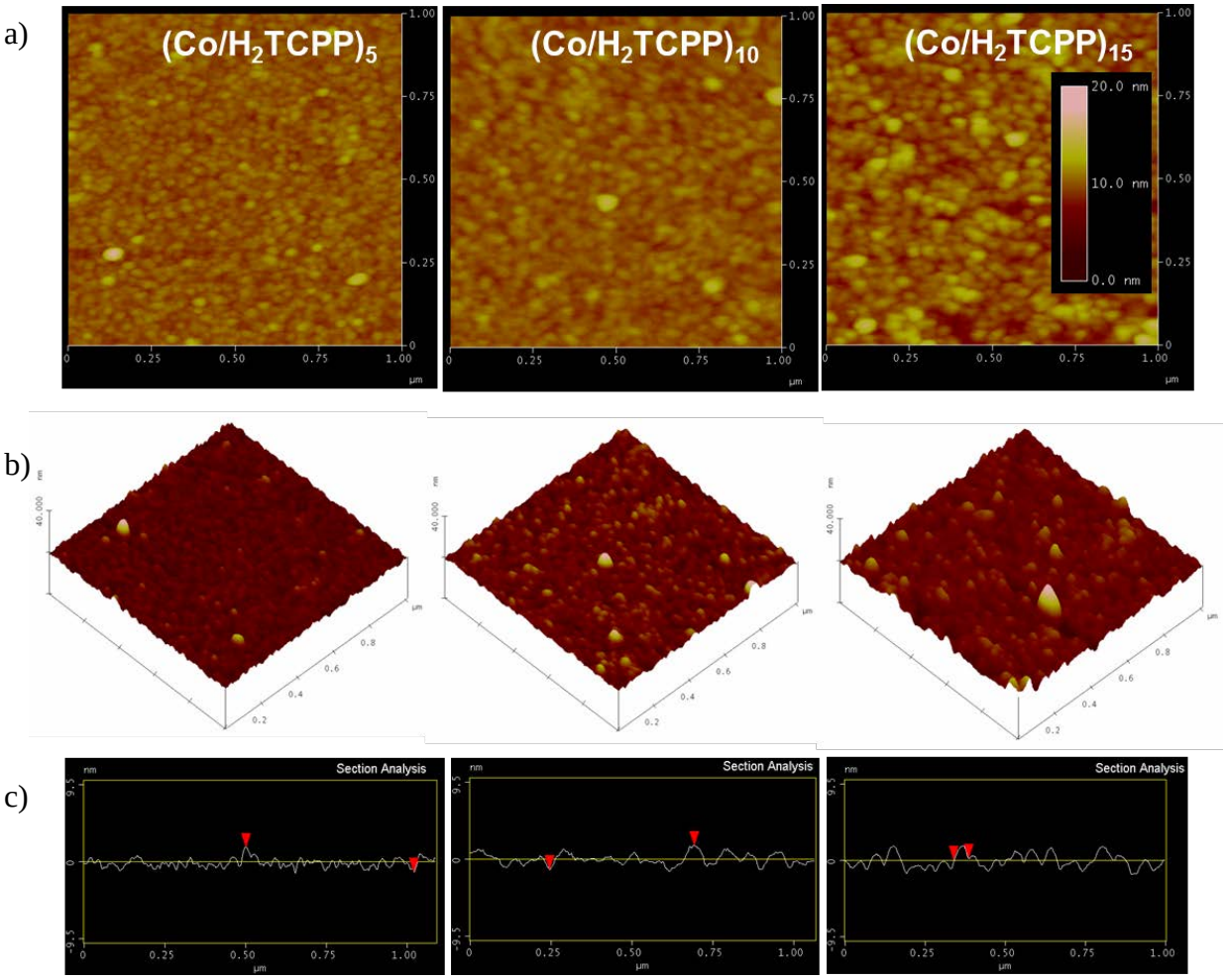


Figure 3. (a) 2D, (b) 3D AFM height image, and (c) section analysis of $(Co/H_2TCPP)_5$, $(Co/H_2TCPP)_{10}$ and $(Co/H_2TCPP)_{15}$ on the APTMS-modified Si wafer substrate respectively; Scan size = 1μm × 1μm ; Data scale 20 nm.

3.2 Determination of Coordination Networks

p-MAIRS was used to investigate the molecular vibration of chemical bonds in both IP and OP vibrational modes in thin film.[18, 19] The p-MAIR spectra are shown in Figure 4a and 4c with corresponding to the number of layers. The intense peaks at 1600 and 1400 cm^{-1} were attributed respectively to asymmetric and symmetric stretching of carboxylate (O–C=O) in thin film.[17, 23, 24] These observations provided the clear evidence for the deprotonation of

carboxylic group (COOH) upon assembly with cobalt ion. These results supported the coordination networks by SIA. Furthermore, the absorbance increased linearly with the number of deposited layers in both IP and OP spectra, which implied the well-growth behavior along with multilayer formation (Figure 4b and 4d).

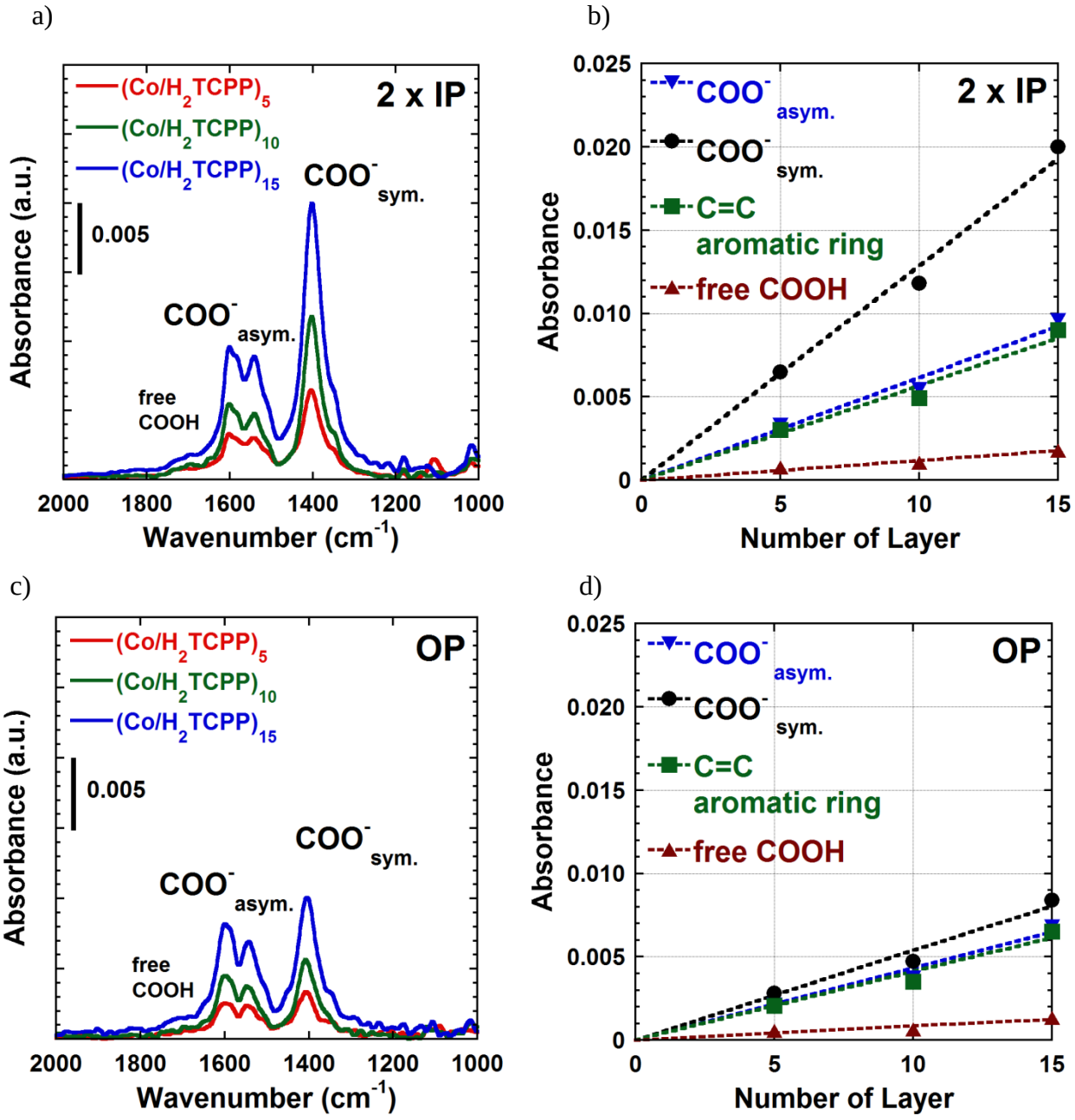


Figure 4. p-MAIR spectra of multilayer film as a number of deposited layers $(Co/H_2TCPP)_5$, $(Co/H_2TCPP)_{10}$ and $(Co/H_2TCPP)_{15}$ on the APTMS-modified Si wafer substrates in (a) In-plane (2×IP) and (c) Out-of-plane (OP).

Figure S7 shows that the XPS survey scans of multilayer film have been primarily examined. The systematic analysis of XPS results was considered with respect to the multilayer film formation. The attenuation trends of Si2p and O1s peak intensities from substrate signal and the increment of N1s, C1s, and Co2p after layer deposition indicated the growth of coordination networks on the substrate. Figure 5 and S8 show the fine scan spectra with deconvolution.

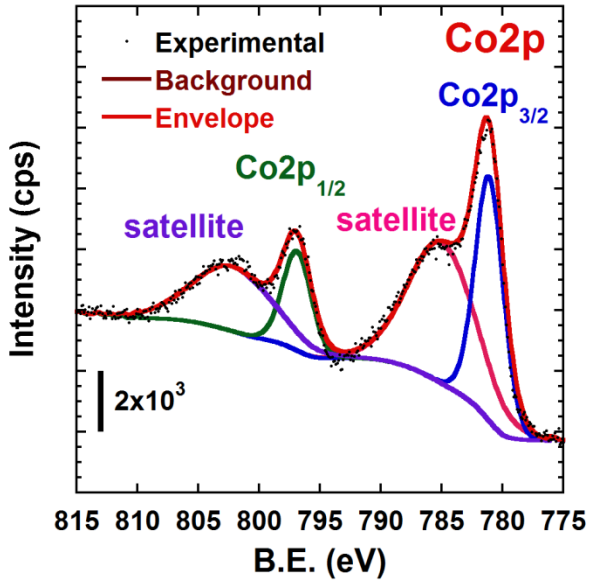


Figure 5. Deconvolution of Co2p spectra of $(Co/H_2TCPP)_{10}$.

For C1s spectra, the fitted peak result showed the presence of COO^- species at 288.1 eV, while the COOH species at 289.4 eV was less observed (Figure S8c).[25, 26] This result shows good agreement with the carboxylate feature from IR spectra. The peaks of $Co2p_{3/2}$ and

$Co2p_{1/2}$ were located at 781.1 and 796.9 eV, respectively[27, 28] along with the presence of the two strong satellite peaks of cobalt at 784.9 and 802.2 eV, representing the oxidation state of cobalt ion as +2 (Figure 5).[29, 30, 31] Furthermore, no difference in Co2p spectra was observed, indicating that the cobalt oxidation number was not changed during fabrication process. The results show the coordination network between cobalt ion and H_2TCPP.

3.3 Structural Alignment of Coordination Networks by SIA

Figure 6a and Table S10 respectively present the PXRD and d-value of three peaks in the bulk sample ($(Co/H_2TCPP)_{Bulk\text{-}2}$). These results suggest that not only the crystalline phase (sharp peaks), but also the amorphous phase (broad peaks) are obtainable in this bulk system. The GI-SAXS profiles and d-value of thin film were taken[32] as shown in Figure 6 and Table S7, respectively. The peak positions of the thin films were completely different from that of the bulk, probably because of the dissimilarity in growth mechanisms or molecular arrangements during network formation on the surface by SIA. In the IP direction, the first weak diffraction peak with a d-value of around 1.9 nm was observed in all thin films. However, the broad and weak peaks indicate the presence of the low degree of molecular ordering. The improvement of molecular ordering in thin films occurred with increasing number of layers. The growth behavior in multilayer films represented high reproducibility with anisotropic properties. We systematically considered the possible structure of thin film on the surface using XRR, AFM, and GI-SAXS results. Particular attention was devoted to four para-carboxyphenyl structures of porphyrin, as shown in Figure 7. It was highly possible to bind at the surface with one or two carboxyl groups[33, 34], whereas the four binding points (parallel or face-on; Figure 7(a)) were less possible because of the difficulties of coordination geometry between cobalt ion and four para-carboxyl groups. Consequently, the single and double anchoring modes can be proposed (Figure 7 (b), (c), (d) and (e)). We further

considered the molecular packing of porphyrin. The double-anchor binding mode (Figure 7(c) and (e)) provides more fixable binding geometry on the surface. This geometry might engender more random arrangement than that provided by the well-organized structure. In contrast, the single-anchor binding mode can freely rotate on the surface, suggesting the possibility for hexagonal packing (Figure S9). Base on the above proposal, we proved this concept by calculation through considering of the porphyrin dimension with cobalt binding moiety that the diameter for its rotation is expected to be ca. 2.2-2.3 nm. Figure S9(c) shows that this proposed model was well supported by the IP diffraction peak of GI-SAXS with a d-value of 1.9 nm. The perpendicular (or edge-on) arrangement of single-anchor configuration (2.3 nm) (Figure 7(b)) was discarded because of the higher repeating length of porphyrin unit than the experimental thickness per layer (1 nm) from XRR and AFM analysis (Table S8). Therefore, the tilting growth with respect to the surface may dominate the structure (Figure 7(d)). The tilting angle can be calculated based on thickness from XRR approximately 60° with respect to the surface normal (Table S9 and Figure S10(a)). This result agrees well with some reported tilted porphyrin arrays of thin films.[21, 35-38]

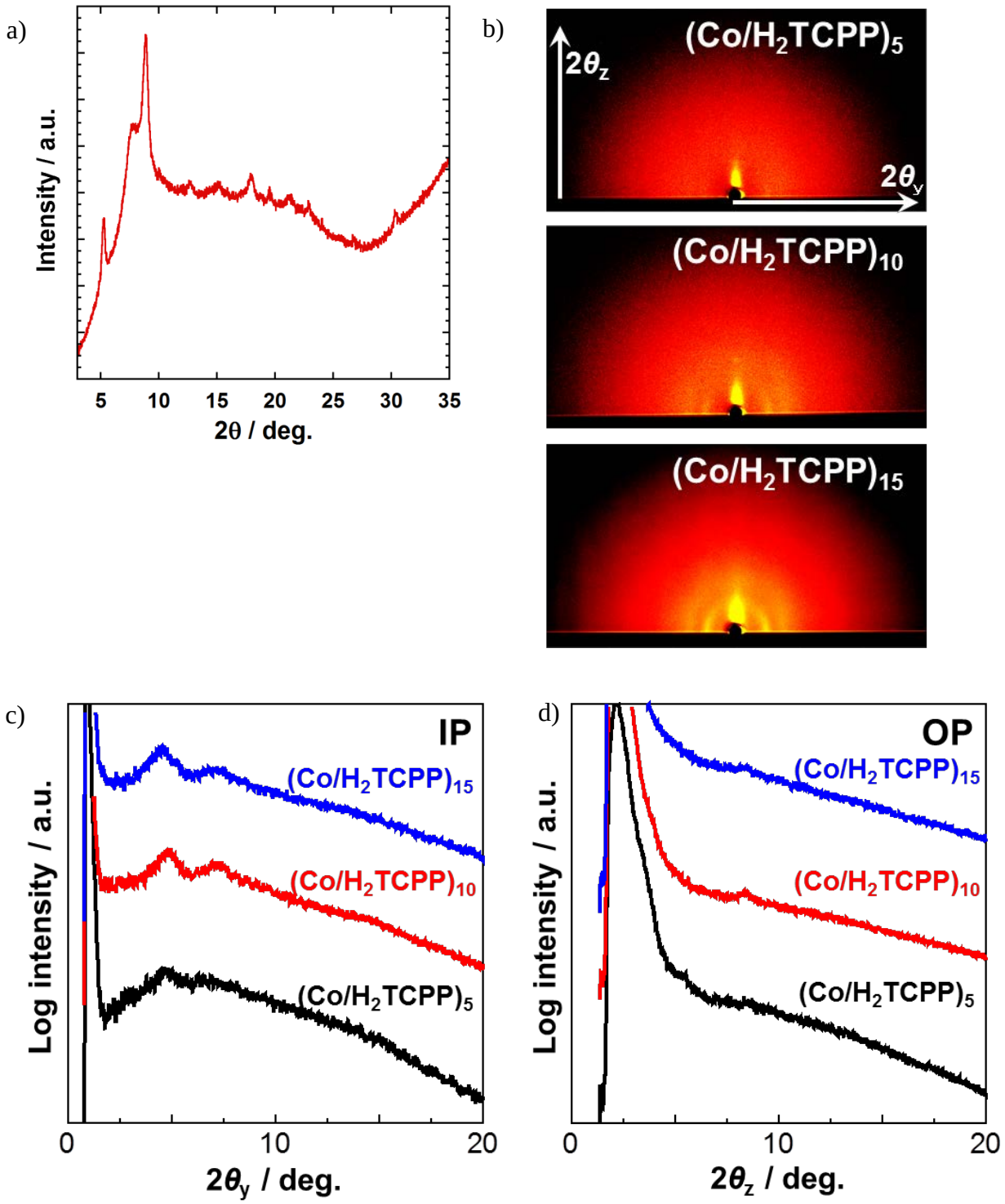


Figure 6. (a) PXRD pattern of bulk ($(Co/H_2TCPP)_{Bulk\text{-}2}$), (b) 2D GI-SAXS profile of multilayer film $(Co/H_2TCPP)_5$, $(Co/H_2TCPP)_{10}$ and $(Co/H_2TCPP)_{15}$ on the APTMS-

modified Si wafer substrates. (c) and (d) 1D GI-SAXS profiles in in-plane (IP) and out-of-plane (OP), respectively.

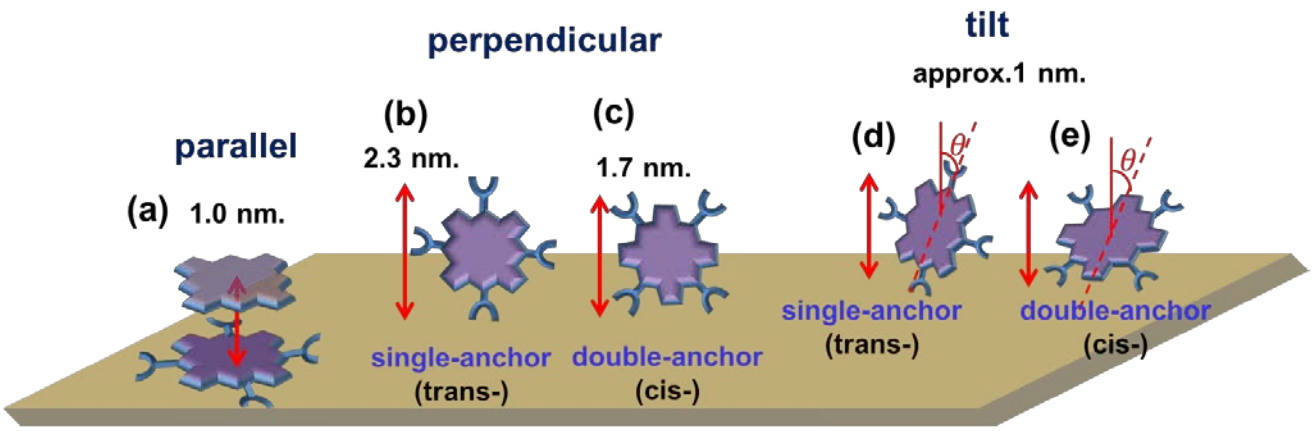


Figure 7. The different molecular models aligned on surface with repeating length (nm) of porphyrin unit with cobalt coordination as denoted as (a) parallel, (b) perpendicular with single-anchor (trans-), (c) perpendicular with double-anchor (cis-), (d) tilt with single-anchor (trans-) and (e) tilt with double-anchor (cis-). The cobalt atom has been omitted from the scheme for the clarity.

In this coordination network system, the well-organized structure and unique thin film on the surface can be effectively achieved using SIA approach even in room temperature conditions. Results suggested that the SIA technique has a powerful ability to control not only the film thickness, but also the structural arrangement on the surface. The structural dissimilarity between the bulk and thin film occurs because of the contribution from SIA method. The step-by-step growth between organic building unit and metal ion on the surface can provide controllable structures. These phenomena are distinct from the bulk situation, for which the coordination architecture between organic molecule and metal ion can occur concurrently. The SIA approach can contribute efficiently to building up of the variety of

molecular conformations. Consequently, novel structures on the surface can be expected and explored using this assembly technology. The design of metal-organic coordination network thin film with controllable growth behavior persists as an important challenge that must be addressed to promote these solid state phenomena for nanoscale device. The interior perspective for the molecular growth manner is highly necessary to elucidate the growth mechanisms along with the development of material properties for specific applications.

4. CONCLUSIONS

The aligned porphyrin-based multilayer film on the substrate can be afforded efficiently through the metal-organic coordination networks using cobalt ion and porphyrin precursors. The thin film growth was controllable using a potential bottom-up approach such as SIA at room temperature with no catalyst. Stepwise growth with compact packing and homogeneous surface was effectively feasible. The mass density of film was almost constant throughout the multilayer structure along with the presence of periodic structure, indicating a well-organized structure of film growth. The alignment of the porphyrin macrocycle plane of the framework has been proposed as a hexagonal packed model using single-anchor binding with tilting of approximately 60° relative to the surface substrate. The structure of the synthesized thin film was distinct from the bulk synthesis, which suggests a significant role of the surface for the coordination network formation. This technique of nanostructure fabrication on the surface provides high probability to promote the unique structure and develop the material properties for the desirable applications.

ASSOCIATED CONTENTS

Supporting Information.

Supporting information provides additional details including those related to the following: UV-Vis, XRR, AFM, FTIR, XPS, GI-SAXS, structural alignment on surface, the reported porphyrin network, and synthesis and characterization of bulk samples ($(Co/H_2TCPP)_{bulk}$). These materials are available free of charge via the internet at http://pubs.acs.org.

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Notes

The authors have no conflict of interest, financial or otherwise, in relation to this study.

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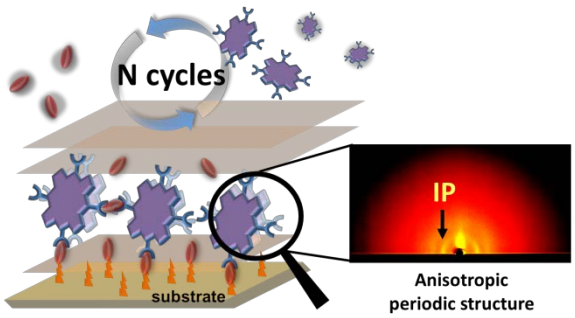
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