

Macromolecular Research

www.springer.com/13233
pISSN 1598-5032 eISSN 2092-7673

DOI 10.1007/s13233-((will be filled in by the editorial staff))

***Corresponding Authors:**

E-mail: majoral@lcc-toulouse.fr

Tel.: (+)33 5 61 33 31 00

Fax: (+)33 5 61 55 30 03

Address: Laboratoire de Chimie de Coordination, CNRS, 205 route de Narbonne, F-31077 Toulouse Cedex, France

E-mail: wolfgang.knoll@ait.ac.at

Tel.: +43 50550 4002

Fax: +43 50550 4000

Address: AIT Austrian Institute of Technology, Donau-City-Strasse 1, 1220 Vienna, Austria

E-mail: dhkim@ewha.ac.kr

Tel.: (+) 82 2 3277 4517

Fax: (+) 82 2 3277 3419

Address: Department of Chemistry and Nano Science, Division of Molecular and Life Sciences, College of Natural Sciences, Ewha Womans University, 52, Ewhayeodae-Gil, Seodaemun-Gu, Seoul 03760, Korea

Layer-by-Layer Self-Assembly of Bisdendrons: An Unprecedented Route to Multilayer Thin Films

Ok-Joo Lee,^{1,§} Valérie Maraval,² Anne-Marie Caminade,² Kyungwha Chung,³ King Hang Aaron Lau,⁴ Kwanwoo Shin,⁵ Jean-Pierre Majoral,^{*,2} Wolfgang Knoll^{*,6} and Dong Ha Kim,^{*,3}

¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

²Laboratoire de Chimie de Coordination, CNRS, 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex, France

³Department of Chemistry and Nano Science, Division of Molecular and Life Sciences, College of Natural Sciences, Ewha Womans University, 52, Ewhayeodae-gil, Seodaemun-gu, Seoul 03760, Korea

⁴Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

⁵Department of Chemistry, Interdisciplinary Program of Integrated Biotechnology, Sogang University, 35, Baekbeom-ro, Mapo-gu, Seoul 04107, Korea

⁶AIT Austrian Institute of Technology, Donau-City-Strasse 1, 1220 Vienna, Austria

[§]Current Address: Korean Intellectual Property Office, Gov. Complex Daejeon, 189, Cheongsa-ro, Seo-gu, Daejeon, 35208, Korea

Received Month Xth, 20XX; Revised Month Xth, 20XX; Accepted Month Xth, 20XX

Abstract: We present an unprecedented route to fabricate multilayer thin films by single component layer-by-layer molecular self-assembly. Tailored water-soluble phosphorus bisdendrons were obtained via core to core assembling of two dendrons bearing anionic groups at one end and quaternizable amino groups at the other end. Adsorption of a 1st bisdendron monolayer on a charged substrate followed by sequential quaternization/deposition of a 2nd layer leads to a stepwise growth of multilayers. By this way homogeneous multilayer thin films were successfully constructed as confirmed by spectroscopic and microscopic analysis.

Keywords: Bisdendron, Layer-by-layer self-assembly, Multilayer thin films, Surface plasmon resonance spectroscopy

1. Introduction

The integration of materials into thin film geometry has been actively pursued in recent nanoscience and nanotechnology. Up to date, various methods have been proposed to fabricate thin films including chemical/physical vapor deposition, sputtering, molecular beam epitaxy, spin coating, Langmuir-Blodgett,

self-assembly, etc. Among these, the layer-by-layer (LbL) self-assembly has been recognized as a versatile bottom-up nanofabrication route to generate thin films with diverse compositions.¹⁻³ This methodology involves the alternate adsorption of oppositely charged molecules driven by electrostatic attraction that allows well-defined multilayer structures on the nanoscale precision in a very controlled way. Such multilayer designs provide access to a wide range of applications in chemical sensors, batteries, luminescent devices, molecular diodes, field-effect transistor gate, anti-reflection coatings, bioactive coatings, drug carriers, and electrochromics.^{4,5} The functional nano-architectures obtained by LbL process, however, generally require at least two oppositely charged polyelectrolytes that lead to heterogeneous structures, which may limit their potential usefulness. Here, we report a new paradigm to fabricate multilayer thin films composed of a single component molecule using conventional LbL deposition technique. The model polyelectrolyte used in this study and the entire scheme for the buildup of multilayer thin films are presented in **Figure 1** and **Figure 2**, respectively. The experimental results and detailed issues are discussed in the following sections.

2. Experimental

2.1. Bisdendron synthesis

Bisdendron molecules with carboxylic acids at one end and amino functional groups at another end were synthesized as reported in our previous study.⁶⁻⁷ In brief, the tailored water-soluble phosphorus bisdendrons were obtained via core to core assembling of two dendrons bearing different groups both at the level of the focal point and at the level of the outer shell. The first dendrons exhibit a vinyl group at the core and either 4 or 8 carboxylate groups on the surface (4 for the dendron of generation 1, 8 for the dendron of generation 2) while the other dendrons incorporate a primary amino group at the focal point and tertiary amino groups (4 or 8) at the periphery. The core-core coupling of these entities involves Michael addition between vinyl and primary amino groups and leads to the bisdendrons **G1** and **G2**.⁷

2.2. LbL deposition of bisdendron

First, a quartz or silicon dioxide (SiO₂) substrate was modified by 3-aminopropyltrimethylsilane (3-APDMES) self-assembled monolayer (SAM) to provide positively charged surface (**Figure 2a**). The cleaned quartz or SiO₂ substrates were exposed to 3-APDMES by evaporating at 130 °C for 2 hours, then ultrasonicated in toluene, acetone, ethyl alcohol and H₂O for 10 min. 3-APDMES modified substrate was immersed in bisdendron solutions of 1 mg/ml concentration in THF/deionized water (50v:50v) for 1h and subsequently washed with THF/H₂O mixed solvent to eliminate the excess molecules. Substrate prepared in this way was rinsed to remove any physically adsorbed molecules. At this step, carboxylate groups of the bisdendrons were anchored to the positive surface via electrostatic attraction. Next, the neutral amine groups (-N(C₂H₅)₂) exposed at the air surface were converted to positively charged groups (-N⁺(C₂H₅)₂CH₃) by a quaternization reaction with methyl iodide (CH₃I) as shown in Figure 2b.⁸ It should be noted here that reaction temperature plays a critical role in this quaternization reaction.⁹ Concretely, the substrate with the 1st bisdendron layer was dipped into 0.2 mg/ml CH₃I solution at 40 °C for 12 h.¹⁰ For comparison, the resulting surface was rough by fast conversion at higher temperature and the quaternization did not proceed at lower temperature even by prolonged reaction over 48 hours. In order to remove any residual CH₃I present after the quaternization, the film was dried in vacuum at 50 °C for 2 hours. If the extra CH₃I molecules are not removed completely, the residues convert the neutral nitrogen units of the next 2nd bisdendron into positive groups, which in turn induces the self-agglomeration of bisdendrons having both positive and negative functionalities within one unit. As a final step, the 2nd bisdendron layer was adsorbed onto the altered positive surface.

2.3. Characterization

Absorbance spectra were obtained using UV-visible spectrophotometer (Perkin-Elmer, Lambda 9). Surface plasmon resonance (SPR) angular reflectance curves were measured with a home-built SPR setup in which Kretschmann configuration was used with an Au layer evaporated onto a glass substrate (LaSFN9) and a 90° LaSFN9 glass prism ($n = 1.85$ at $\lambda = 632.8$ nm). By varying the angle of incidence the reflected intensity shows a sharp minimum at the resonance angle which depends upon the precise architecture of the metal/dielectric interface. A closed glass flow cell (volume 150 μ L) was fabricated in-house and was used for on-line recording

of adsorption process and for exchanging solutions. The flow cell was conveniently coupled to the gold-prism assembly by the use of elastic O-rings. The Au substrate was first modified by cysteamine monolayer to render a positively charged surface onto which carboxylate groups of the bisdendrons are readily adsorbed. Height contrast atomic force microscopy (AFM) images were measured using Digital Instruments Dimension 3100 scanning force microscope in the tapping mode.

3. Results and Discussion

In order to build up LbL-driven multilayer thin films composed of a single component molecule, we employ symmetric spherical bisdendrons,⁶⁻⁷ two dendrons connected through the core, as building blocks to construct multilayers. The chemical structures of the two types of bisdendrons used in this study are described in **Figure 1a** and **1b** for 1st generation (**G1**) and 2nd generation (**G2**), respectively. Such bisdendrons possess anionic groups on one end in order to ensure solubility in water and easy surface modification via electrostatic interactions, while the other one bearing easily quaternizable amino end groups or any type of functional groups which will bring new properties for the target applications.

A scheme to build multilayers of bisdendrons is depicted in **Figure 2**. The substrate was first modified by 3-APDMES to render a positive charge at the surface. Then, the positively charged substrate was decorated with the bisdendron via the electrostatic attraction between the carboxylate groups of bisdendrons and the ammonium groups at the substrate surface. Prior to the deposition of the 2nd bisdendron, a quaternization reaction was conducted to introduce positive charge at the neutral amine groups of the 1st bisdendron layer. The resulting sample with a bisdendron monolayer was dipped into the bisdendron solution followed by rinsing with deionized water, resulting in the construction of one bilayer. Repetition of the above two steps (**Figure 2a** and **2b**) could lead to homogeneous thin nanostructured multilayers with precisely defined film thickness. The thickness of monolayers composed of **G1** and **G2** bisdendrons was evaluated by surface plasmon resonance (SPR) spectroscopy in static angular mode (**Figure 3**). The thickness of monolayers calculated by Fresnel fitting of the experimental curves, assuming the refractive index of bisdendrons being similar to other dendritic polymers (1.42),¹¹ was ~9 nm for the **G2**. In case of **G1**, The SPR angle shift due to the binding of **G1** was slightly larger than that of **G2**, which is not consistent with the theoretically expected result considering the relationship between the molecular size and SPR angle shift. This observation can be explained by the following reasons. The angular shift due to the binding of the cysteamine layer onto the substrate used for the **G1** deposition was larger than that for the **G2**, implying that the cysteamine molecules were more densely packed for the former case. Second, the larger volume of the **G2** molecules with more bulky branches may cause steric hindrance, resulting in a relatively lower amount of **G2** deposition onto the cysteamine layer.¹² As an alternative way, the thickness of **G1** can be evaluated by comparing the absorbance values (see **Figure 4** below) and it was estimated to be ~3.4 nm assuming the same refractive index. The thickness of multilayers was not evaluated by SPR spectroscopy since the methyl iodide solution used for quaternization dissolves the Au substrates required for generating the surface plasmon.

The multilayers of bisdendrons fabricated on quartz substrates by the above-described scheme were investigated by UV-visible spectroscopy. The UV-visible spectra for the multilayers of **G1** and **G2** as a function of the number of layers were measured by UV-visible spectrophotometer as shown in **Figure 4a** and **4b**, respectively. It is clearly observed that the absorbance increases monotonically with increasing the number of deposition steps. The bulk bisdendrons exhibit three noticeable peaks at 285, 300 and 360 nm at a preliminary measurement. Here, the peak at 285 nm, characteristic of the π - π^* transition of the derivatives from the phenyl group, was used to monitor the growth of multilayers. The linear increase in absorbance around 280 nm with increasing the number of layers verifies that an almost equal amount of bisdendrons was deposited at each deposition step. The overall increase in intensity of the **G2** multilayer (**Figure 4b**) was higher than that of the **G1** multilayer (**Figure 4a**), indicating that **G2** bisdendron with larger size led to optically thicker film.

The surface morphology was investigated by AFM measurements. According to the AFM results, the substrates were uniformly covered by the multilayer films for both **G1** and **G2** bisdendrons over the entire area of the surface (**Figure 5**). With increasing the number of the deposition, more rough surfaces were obtained from

the **G2**-based multilayers compared to the **G1**-based ones, as confirmed by the cross-sectional profiles in **Figure 5c** and **5d** compared to **Figure 5a** and **5b**.

4. Conclusions

In summary, we present a new concept by which homogeneous multilayer thin films could be prepared using a single species of bisdendrons via LbL deposition. Repetitive deposition/modification cycle of the constituent building block, i.e., phosphorus bisdendrons, led to controlled fabrication of multilayers at a molecular level. Spectroscopic and microscopic studies demonstrated that uniform films were successfully generated over the entire area of the substrate with a monotonous growth in film thickness. The unique methodology suggested by this work may open new pathways to develop functional thin film nano-objects not accessible by conventional processes.

5. Acknowledgments

This work was supported by National Research Foundation of Korea Grant funded by the Korean Government (2014R1A2A1A09005656). Prof. J.-P. Majoral, Prof. A.-M. Caminade and Dr. Valérie Maraval thank the Centre National de la Recherche Scientifique (CNRS, France) for financial support.

6. References

- (1) G. Decher, *Science*, **277**, 5330, 1232-1237 (1997).
- (2) G. Decher; J. D. Hong; J. Schmitt, *Thin Solid Films*, **210**, 831-835 (1992).
- (3) F. Caruso; R. A. Caruso; H. Möhwald, *Science*, **282**, 5391, 1111-1114 (1998).
- (4) P. T. Hammond, *Adv. Mater.*, **16**, 15, 1271-1293 (2004).
- (5) C. Jiang; V. V. Tsukruk, *Adv. Mater.*, **18**, 7, 829-840 (2006).
- (6) A.-M. Caminade; A. Maraval; J.-P. Majoral, *Eur. J. Inorg. Chem.*, **2006**, 5, 887-901 (2006).
- (7) V. Maraval; A. Maraval; G. Spataro; A.-M. Caminade; J.-P. Majoral; D. H. Kim; W. Knoll, *New J. Chem.*, **30**, 12, 1731-1736 (2006).
- (8) E. M. Arnett; R. Reich, *J. Am. Chem. Soc.*, **102**, 18, 5892-5902 (1980).
- (9) V. Bütün; S. P. Armes; N. C. Billingham, *Macromolecules*, **34**, 5, 1148-1159 (2001).
- (10) The boiling point of CH₃I is about 43 oC.
- (11) T. D. Lazzara; K. H. A. Lau; A. I. Abou-Kandil; A.-M. Caminade; J.-P. Majoral; W. Knoll, *ACS Nano*, **4**, 7, 3909-3920 (2010).
- (12) M. Kim; S. Schmitt; J. Choi; J. Krutty; P. Gopalan, *Polymers*, **7**, 7, 1346-1378 (2015).

Schemes and Figures

((Captions))

Figure 1. Chemical structure of the bisdendrons used to construct multilayer thin films in this study: (a) 1st generation (**G1**); (b) 2nd generation (**G2**).

Figure 2. Schematic illustration to generate multilayer thin films of bisdendrons by layer-by-layer self-assembly strategy: (a) adsorption of the 1st bisdendron layer onto a positively charged surface; (b) quaternization of neutral nitrogens on the surface of the first bisdendron layer with CH_3I to render positively charged terminal groups; (c) Adsorption of the 2nd bisdendron layer onto the positively charged surface of the 1st bisdendron layer.

Figure 3. Scan mode SPR profiles of the deposition of **G1** (a) and **G2** (b) monolayers (red curves) onto Au substrates modified by cysteamine (green curves) monolayers.

Figure 4. UV-visible absorption spectra of bisdendron multilayers of **G1** (a) and **G2** (b) on quartz plates with a different number of deposition steps $n = 1-4$ (from lower to upper curves). The inset shows the dependence of the absorbance of the peak at 285 nm on the number of deposition steps.

Figure 5. AFM images of 2 layers of **G1** (a) & **G2** (b) bisdendrons, and those of 4 layers of **G1** (c) & **G2** (d) bisdendrons fabricated on silicon dioxide substrates modified by 3-APDMES monolayers.

((Figures))

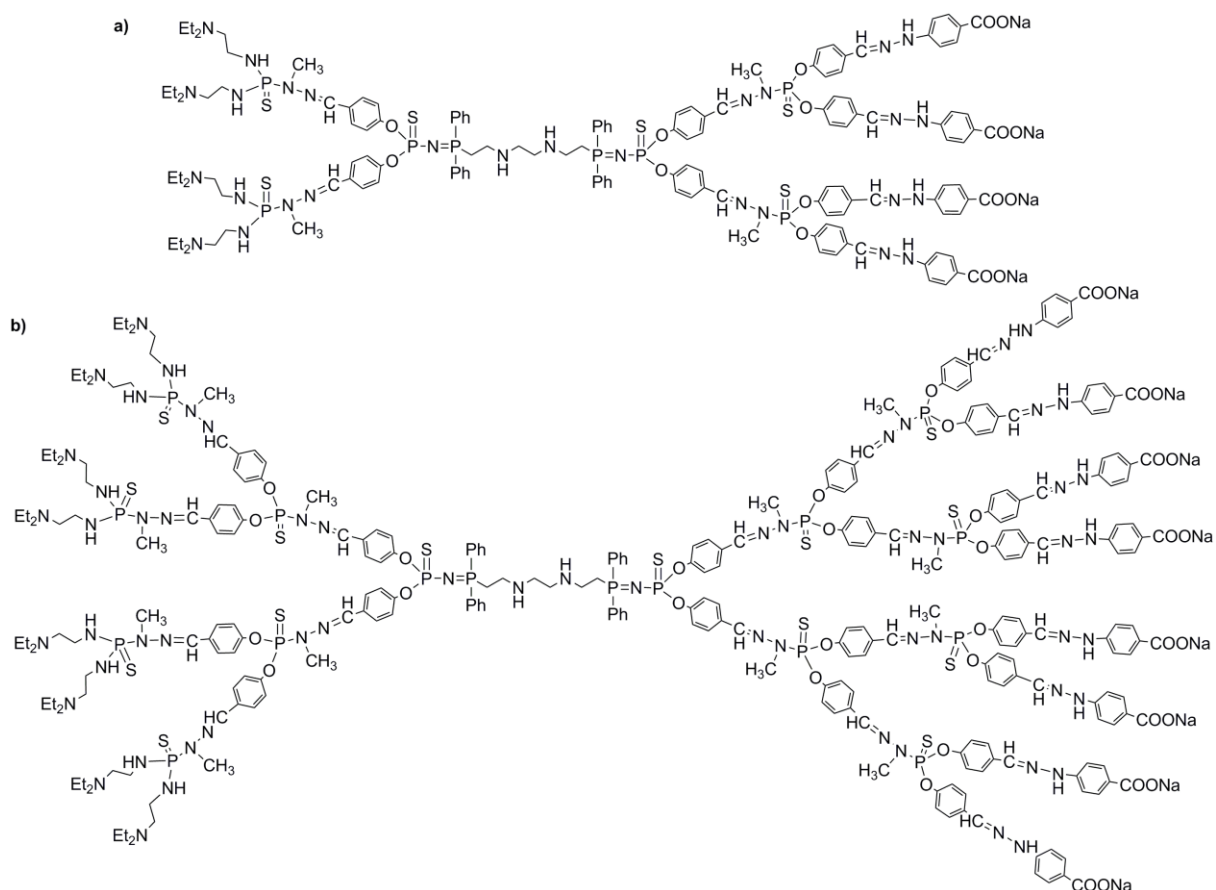
Figure 1.

Figure 2.

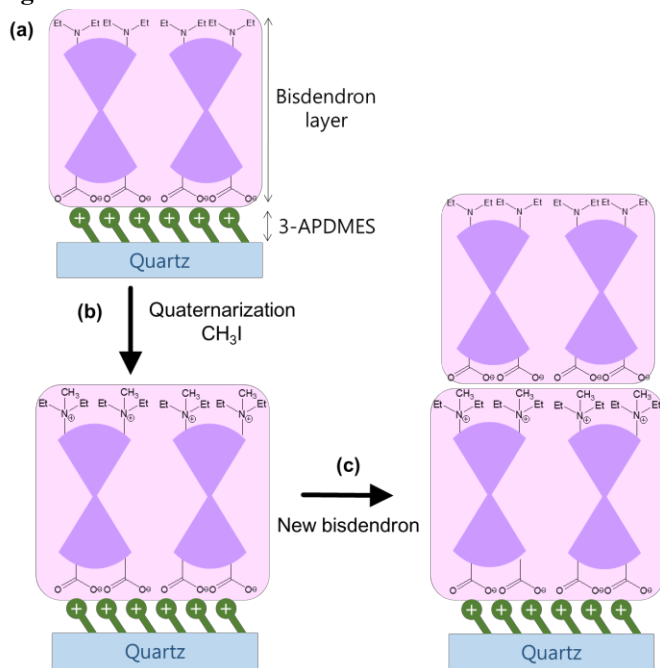


Figure 3.

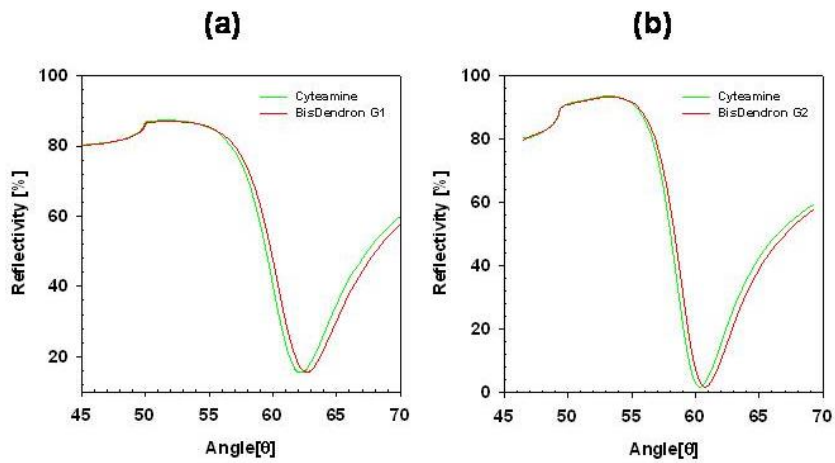


Figure 4.

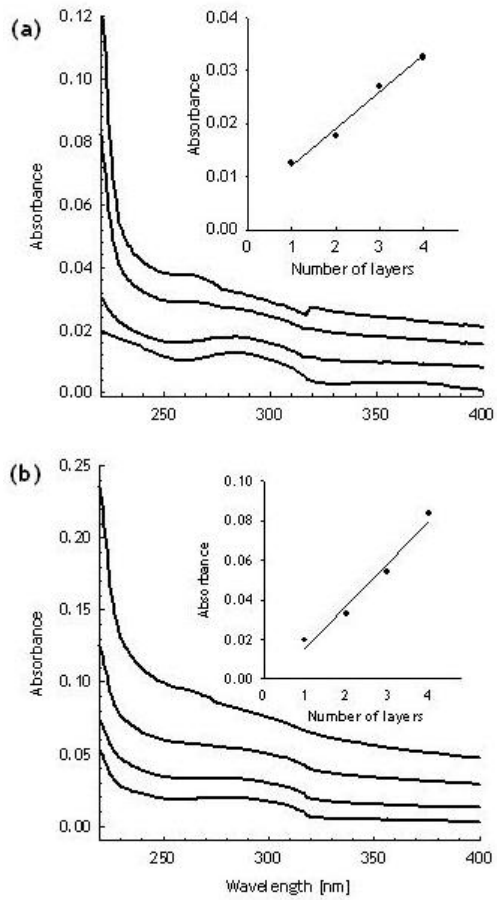


Figure 5.

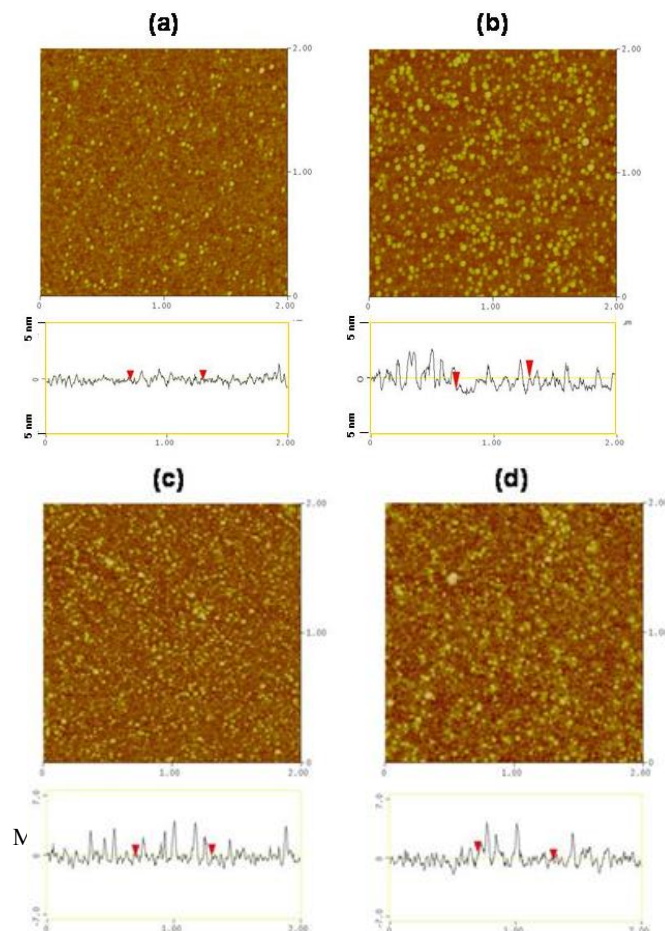


Table of Contents

Layer-by-Layer Self-Assembly of Bisdendrons: An Unprecedented Route to Multilayer Thin Films

Ok-Joo Lee, Valérie Maraval, Anne-Marie Caminade, Kyungwha Chung, King Hang Aaron Lau, Kwanwo Shin, Jean-Pierre Majoral*, Wolfgang Knoll* and Dong Ha Kim*

Macromol. Res., **XX**, XXX (20XX)

We present an unprecedented route to fabricate multilayer thin films composed of a single component molecule by layer-by-layer self-assembly strategy. Tailored water-soluble phosphorus bisdendrons were obtained via core to core assembling of two dendrons bearing anionic groups at one end and quaternizable amino groups at the other end. Adsorption of a 1st bisdendron monolayer on a charged substrate followed by sequential quaternization/deposition of a 2nd layer leads to a stepwise growth of multilayers. By this way homogeneous multilayer thin films were successfully constructed as confirmed by spectroscopic and microscopic analysis.

