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Linear vs Exponential Formation of Molecular-Based Assemblies

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Abstract: Here we present the critical role of the molecular structure and reaction parameters on the nature of thin-film growth, using a versatile two-step assembly method with organic and metal−organic chromophores cross-linked with palladium. It was found that the polypyridyl complexes exhibit exponential growth, whereas, under identical conditions, the organic systems exhibit linear behavior. The internal film morphology plays a pivotal role in the storage and usage of the palladium, where a more porous structure results in exponential growth. Interestingly, through proper tuning of the reaction conditions, the growth of the molecular assemblies can be controlled, resulting in a changeover from exponential to linear growth. These findings unequivocally demonstrate the importance of both the internal film structure and deposition conditions on the assembly of molecular-based films.

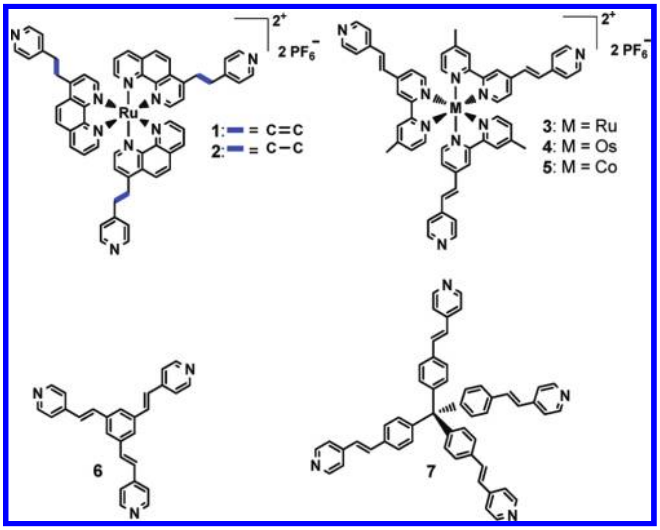
Stepwise assembly of thin films is an intriguing approach for designing, controlling, and understanding the structure and function of organic and metal−organic materials at the molecular level.[1] Generally, the physicochemical properties of such assemblies increase linearly with the number of deposition cycles. Growing thin films nonlinearly has been reported with several polyelectrolytes[2] and alkylsilanes.[3] Given its success, it is highly desirable to expand this phenomenon to the assembly of other functional films using less deposition steps in comparison to conventional methods. This approach might lead to the generation of new redox-active interfaces that can operate as electrochromic or photovoltaic materials and mimic the behavior of various logic circuits, including flip-flops.[4] Until now, only one example has been reported of a functional molecular-based self-propagating assembly.[5] This process involves the alternate deposition of a polypyridyl osmium complex and a palladium precursor from solution. The surface-bound assembly is actively involved in its own formation since it is able to store and use the palladium to bind osmium complexes in a nonlinear fashion.

The present study demonstrates that the nature of molecular-based thin film assembly (i.e., linear vs exponential growth) can be systematically controlled by varying the structure of the molecular component and by varying the reaction conditions. A series of molecular building blocks (Chart 1, **1**−**7**) was used to probe various parameters, including the effect of the metal ion (Ru, Os, Co), ligand periphery, rigidity/flexibility of the binding sites, and overall geometry and symmetry of the molecules.

A **1**-based template layer, chemically attached to the substrate surface, was used for forming all the assemblies. This layer was formed by reacting chlorobenzyl-terminated monolayers on glass, quartz, ITO, and silicon substrates (0.8 cm ×2.5 cm) with complex **1** in solution at elevated temperatures. The template layer was characterized by UV−vis spectroscopy, spectroscopic ellipsometry, XPS analysis, cyclic voltammetry, and semicontact AFM (Figures S1−S3 and Tables S1−S2). For instance, XPS analysis revealed the formation of a pyridinium salt by quaternization of one out of three pyridyl moieties (N_{1s} 399.8 eV, N^{+}_{1S} 401.4 eV; $N_{total}/Ru = 9:1$, $N/N^{+} = 8:1$). Ellipsometry showed a thickness of 1.4 ± 0.3 nm, and the AFM derived $R_{rms} \approx 0.7$ nm for 500 nm ×500 nm scan areas are indicative of a relatively smooth and homogeneous template layer.

The molecular-based assemblies were generated at room temperature in air by iterative immersion of the **1**-based template layers into a solution of $PdCl_2(PhCN)_2$ in THF and a solution of one of the chromophores (**1**−**7**, shown in Chart 1) in THF/DMF (9:1, v/v). The benzonitrile ligands of the palladium precursor are readily replaced by coordination of the pyridyl groups. The functionalized substrates were thoroughly washed after each deposition step by sonication in various organic solvents to remove any physisorbed materials. We have shown that pyridyl-palladium coordination is a versatile structural unit for forming various surface-bound structures.[5,6]

Chart 1. Molecular Structures of Compounds **1**−**7**[a]



[a] For synthesis and characterization, see the Supporting Information.

The film growth progress was monitored *ex situ* by UV−vis spectroscopy and by ellipsometry (Figures 1, S4, and S5). Interestingly, the absorption intensities of the metal-to-ligand charge-transfer (MLCT) bands and the thickness of all the assemblies based

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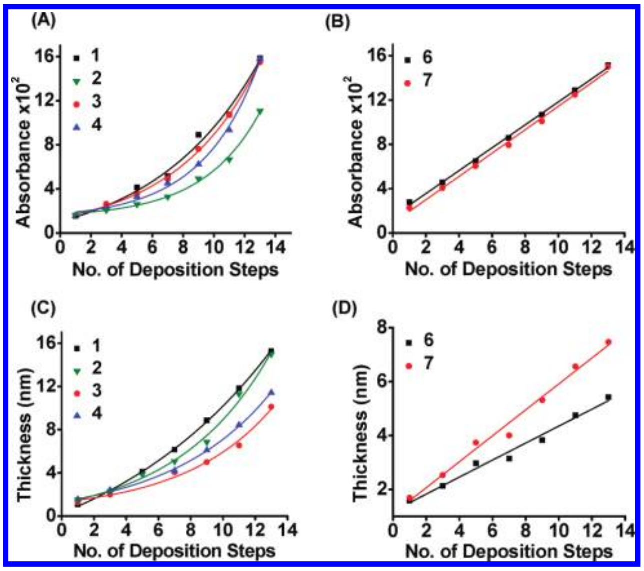

Figure 1. (A) Exponential dependence of the intensities of the assembly MLCT bands for **1**: 500 nm, **2**: 452 nm, **3**: 491 nm, **4**: 510 nm vs the number of deposition steps. (B) Linear dependence of the intensities of the assembly absorption bands for **6**: 337 nm and **7**: 344 nm vs the number of deposition steps. (C) Exponential dependence of the film thickness with complexes **1**−**4** vs the number of deposition steps. (D) Linear dependence of the film thickness with chromophores **6**−**7** vs the number of deposition steps. $R^2 \geq 0.98$ for all fits. UV−vis spectra are shown in Figure S4. The data of the **5**-based assembly (21 deposition steps) is shown in Figure S5.

on polypyridyl complexes (**1**−**5**) increase exponentially (Figures 1A,C, S5). In contrast, a linear correlation was observed for the organic chromophores **6** and **7** (Figure 1B,D). These observations suggest that the exponential growth is not influenced by the metal center (**3**: Ru, **4**: Os, **5**: Co) and ligand framework (**1**: C=C vs **2**: C−C; **1**: phenanthroline vs **3**: bipyridine). Apparently, the linear behavior is not affected by the molecular geometry and symmetry (**6**: planar, C_{3h} vs **7**: tetrahedral, T_d) and number of coordination sites (**6**: 3, **7**: 4). The structural regularity of all systems is further demonstrated by the linear relationship of the thicknesses vs the absorption intensities (Figure S6). Regularly growing assemblies are obtained for all seven chromophores whereas the type of the molecular components used (**1**−**5** and **6**−**7**) is expressed in the growth mode of the assembly. AFM analyses revealed similarly smooth film surfaces for the fully formed assemblies (13 deposition steps; $R_{\rm rms} \approx 0.6$ nm; Figure S7), suggesting that the roughness and surface morphology do not play a major role in controlling the growth process.

Exponential growth in a two-step deposition process requires an excess of one of the components to remain in the assembly or on the assembly surface, where it is used during the sequential deposition step of the second component.[2,3,7] Further insight into our linear vs exponential growth processes was obtained by angle-resolved XPS. These measurements were performed with representative **1**- and **7**-based assemblies (Figure 2A). Interestingly, for the **1**-assemblies the Pd/N ratio is affected by the nature of the deposition step. For instance, after the deposition of chromophore **1**, the Pd/N atomic concentration ratio of the **1**-based assembly was found to be higher by ~44% than the value expected for an ideal network. In contrast, it was found to be 104% higher than expected after exposing this assembly to a solution of the Pd precursor. The homogeneously distributed storage of excess Pd is also evident from the Pd/Ru ratio (Figure S8). The Pd/N ratio of the **7**-based assembly remained close to the ideal value for a fully formed network irrespective whether the assembly was exposed to a solution with an excess of $PdCl_2(PhCN)_2$ or chromophore **7**.

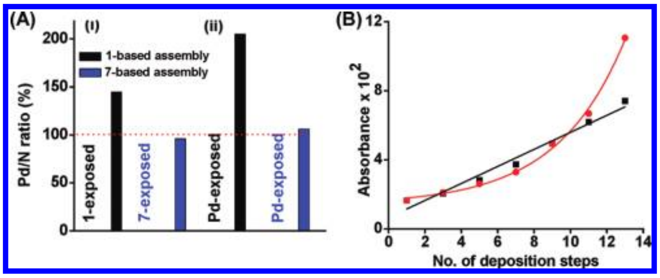

Figure 2. (A) Angle-dependent XPS-derived Pd/N ratios for (i) **1**- and **7**-based assemblies (13 deposition steps) and (ii) after an additional Pd deposition step. The theoretical Pd/N ratios for fully formed networks are 0.17 (**1**) and 0.50 (**7**), which have been normalized to 100% (red dots). (B) Exponential (red trace) and linear dependence (black trace) of the intensities of the MLCT band of the **2**-based assembly at $\lambda = 452$ nm vs the number of deposition steps upon exposure to $PdCl_2(PhCN)_2$ for 15 and 5 min, respectively. $R^2 \geq 0.97$ for both fits.

The linearly growing network cannot store, under the applied reactions conditions, an excess of palladium that can be used for self-propagating assembly. Although the reason for the differential behavior between the polypyridyl complexes (**1**−**5**) and the organic chromophores (**6**−**7**) is not straightforward, it is likely that the latter systems have an optimal geometry to form saturated and dense networks. The cationic complexes most probably form porous structures and allow the incorporation of the excess of palladium.[5] It also suggests that the polypyridyl complex (**1**−**5**)-based assemblies might exhibit dynamic/adaptive behavior, whereas the organic chromophores (**6**−**7**) form relatively rigid structures. To demonstrate that the storage of palladium indeed plays a vital role in the exponential film growth, we built-up a **2**-based assembly using a shorter reaction time for the palladium deposition step (5 min instead of 15 min). Remarkably, UV−vis spectroscopy revealed linear growth with $R^2 = 0.97$, with the final assembly having ~60% of the absorption intensity value at $\lambda = 452$ nm of the exponentially growing assembly (Figure 2B).

In summary, this first systematic study of molecular-based self-propagating assemblies underscores the structure of the molecular component as a critical parameter for the storage and usage of palladium. Moreover, it is possible to control the nature of the growth by varying only one reaction parameter (e.g., time) while other variables are held constant. This observation is in agreement with the exponential growth of some polyelectrolyte-based films,[2,7] suggesting that a similar mechanism might be operating.

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Supporting Information Available: Synthesis and characterization data of the compounds, details of the assembly process, additional figures, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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