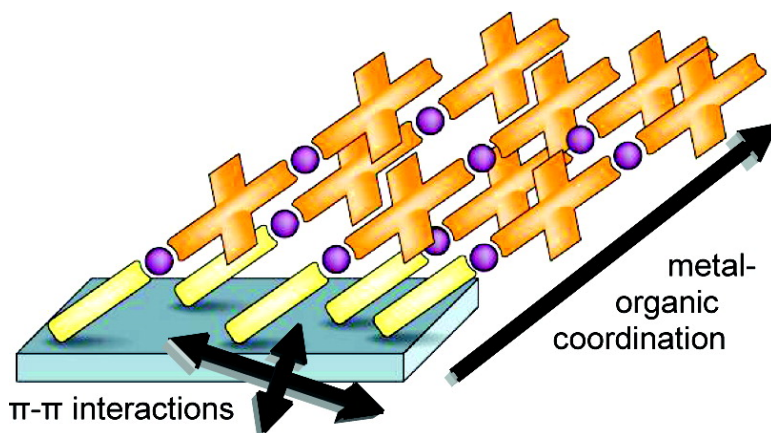


## Molecular Assembly of a 3D-Ordered Multilayer

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## Molecular Assembly of a 3D-Ordered Multilayer

Marc Altman,<sup>†</sup> Olena Zenkina,<sup>†</sup> Guennadi Evmenenko,<sup>‡</sup> Pulak Dutta,<sup>‡</sup> and  
Milko E. van der Boom<sup>\*†</sup>

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, 76100, Israel,  
and Department of Physics and Astronomy and the Materials Research Center,  
Northwestern University, Evanston, Illinois 60208-3113

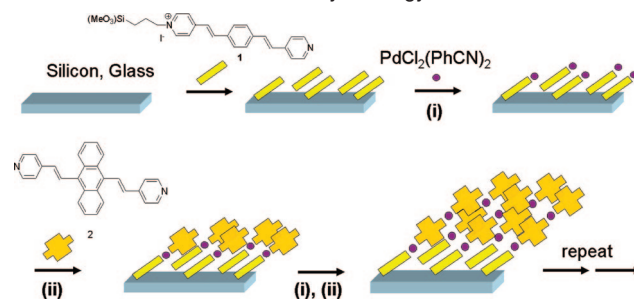
Received January 23, 2008; E-mail: milko.vanderboom@weizmann.ac.il

The structure and properties of organic assemblies are neither easily controlled nor governed by a self-evident set of rules.<sup>1</sup> These are often dictated by geometrical demanding noncovalent forces such as  $\pi$ - $\pi$  interactions.<sup>2</sup> The ability to grow ordered organic materials directly on common substrates permits their incorporation into semiconductor-based technologies.<sup>3</sup> Layer-by-layer solution-based deposition of well-defined organic compounds upon a "self-assembled" monolayer has expanded the range of functional materials with a high degree of order and structural control at the molecular level.<sup>4</sup> A variety of such assemblies has been reported, often based on siloxane-based chemistry or on metal-ligand coordination.<sup>5</sup> An in-depth understanding of the relationship of molecular orientation and interactions with material properties are vital for rational functional design, but studies aimed at understanding film properties resulting from molecular interaction of analogous compounds are rare.<sup>6</sup> We report here a highly ordered molecular-based material using a hierarchical approach where the stronger metal-organic coordination governs the order in the direction of growth and the weaker, sterically demanding,  $\pi$ - $\pi$  interactions tune the lateral stability.<sup>7</sup>

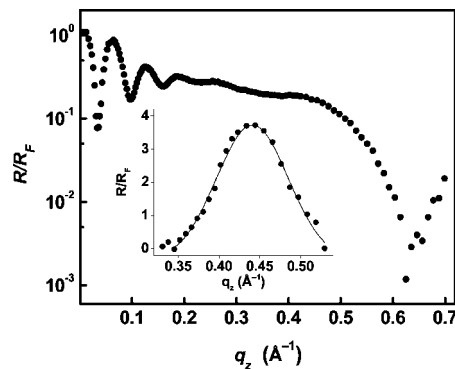
Our recently reported assembly strategy involves iterative coordination of a pyridyl-terminated chromophore and PdCl<sub>2</sub> on a covalently bound **1**-based monolayer supported on glass and silicon substrates. Coordination of pyridine derivatives to Pd(II) assures well-ordered structure in the direction of film growth. We use here  $\pi$ - $\pi$  interactions as a secondary directing factor by introducing an anthracene unit functionalized with two vinylpyridine units. The anthracene core affords face-to-face interactions, while its 30° twist relative to the terminal pyridyl groups allows for face-to-edge interactions.<sup>8</sup> The growth of the assembly in the axial direction is now accompanied and affected by the in-plane order induced by the interlocking of the chromophores. Our iterative wet-assembly methodology was used to deposit eleven alternating layers of PdCl<sub>2</sub> and compound **2** on a covalently bound template layer (Scheme 1).<sup>9</sup>

The film is densely packed with an XRR-determined footprint of 50 Å<sup>2</sup> for each chromophore 2-PdCl<sub>2</sub> unit.<sup>9</sup> Long-range ordering, with a spacing of 14.2 Å, is shown by a Bragg diffraction peak at  $q = 0.44$  Å<sup>-1</sup> (Figure 1). Bragg peaks are rare for molecular-based assemblies, even though it would be expected for any highly ordered film with uniform deposition in each layer.<sup>10</sup> Figure 2 shows the Patterson representation of the XRR data shown in Figure 1. The large primary maximum is due to the substrate-film and film-gas interfaces; that is, its position indicates the overall thickness of the film of ~100 Å.

**Scheme 1.** Schematic of Assembly Strategy<sup>a</sup>



<sup>a</sup> The structure and function of the entire covalently bound assembly is determined by a combination of metal-ligand coordination and  $\pi$ - $\pi$  interactions.



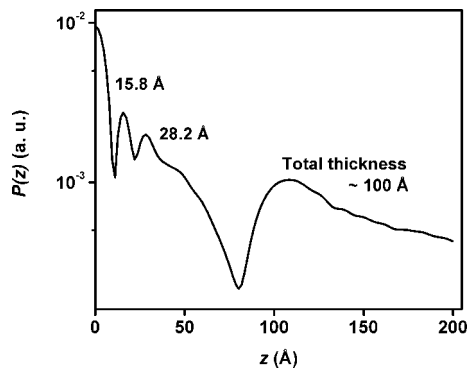
**Figure 1.** XRR spectrum for the multilayer assembly. A Bragg peak, demonstrating the highly regular structure in the axial direction, can be discerned at  $0.44$  Å<sup>-1</sup>. Inset shows the Bragg peak after baseline subtraction.

The secondary maxima show, without any model-dependent assumptions, that there are highly regular electron density variations inside the film with a scale corresponding to the layer ordering that was obtained from the Bragg peak position.

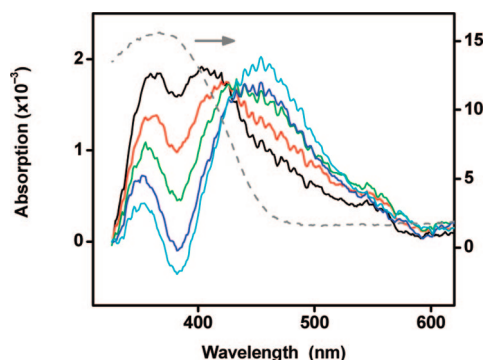
The three-dimensional order controls the optical properties of the assembly as reflected by UV-vis spectroscopy (Figure 3). The uniform growth is confirmed by the linear increase of the ligand to metal charge transfer (LMCT) band at  $\lambda = 250$  nm (Figure 4a).<sup>11</sup> The lateral interactions are evident from the large progressive spectral changes: (i) a bathochromic shift from  $\lambda = 410$  to  $\lambda = 463$  nm, (ii) a decrease in intensity at  $\lambda = 360$  nm, and (iii) a hypsochromic shift from  $\lambda = 364$  to  $\lambda = 349$  nm (Figure 4b). These strong  $\pi$ - $\pi$  interactions between the molecules along the axis of the assembly growth, consistent with the tight molecular footprint, complement the metal-chromophore coordination. Such optical effects are observed in organic

<sup>†</sup> The Weizmann Institute of Science.

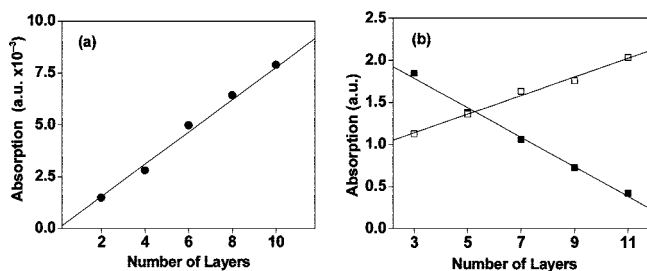
<sup>‡</sup> Northwestern University.



**Figure 2.** Patterson function of the multilayer assembly presented in Figure 1, showing the inherently ordered layered structure in the length-scale domain.



**Figure 3.** Absorption vs wavelength for the visible region for 3 (black), 5 (red), 7 (green), 9 (dark blue), and 11 (light blue) layers. The absorption of the template layer formed of **1** (---, right axis), has been subtracted. The “negative absorption” at 380 nm is a result of this arithmetic.



**Figure 4.** UV-vis absorption vs number of layers deposited on quartz substrates (after baseline correction) at (a)  $\lambda = 250$  nm for PdCl<sub>2</sub> terminated layers. The plot shows linear correlation between the LMCT band and the number of layers ( $R^2 = 0.992$ ). (b)  $\lambda = 360$  nm (filled squares) and  $\lambda = 454$  nm (open squares) showing linear decrease ( $R^2 = 0.993$ ) and increase ( $R^2 = 0.989$ ), respectively.

crystalline films, formed by epitaxial vapor-phase deposition, engineered such that one layer adheres to the next through the  $\pi$ - $\pi$  interactions.<sup>12</sup> In particular, multilayers of polythiophenes or polycyclic aromatics on single crystal substrates show strong excitonic coupling.<sup>2a,b</sup> Examples of covalently bound monolayers that exhibit strong stacking behavior within a single molecular layer have been reported.<sup>6,13</sup> However, this type of behavior in a three-dimensional assembly where the individual layers are chemically bound is unknown.

We have shown that it is possible to achieve a 3D-ordered molecular-based multilayer by a combination of forces consisting of strong metal-ligand coordination and  $\pi$ - $\pi$  interactions.

The organization of the assembly is reflected by XRR, as well as by the optical properties. In particular, metal coordination generates well-defined surface-bound oligomers, which are further stabilized through  $\pi$ - $\pi$  interactions. These interactions are interdependent as the in-plane ordering induces structural regularity in the axial direction: XRR analysis of an analogous assembly lacking in-plane stabilization showed no diffraction.<sup>9</sup> This assembly strategy for new hybrid metal-organic materials mimics the hierarchy of forces that is apparently used by biological systems such as protein-DNA associates for recognition and binding.<sup>14</sup>

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