

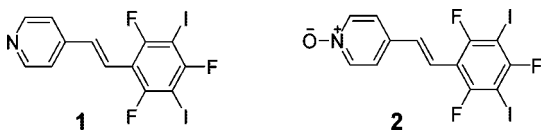
Assembly of Crystalline Halogen-Bonded Materials by Physical Vapor Deposition

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Organic supramolecular assemblies are often based on a combination of noncovalent interactions, including van der Waals forces and π - π stacking, as well as hydrogen bonding (HB).¹ The design of proper molecular synthons with well-defined HB functionalities requires accurate control over the corresponding film microstructure. HB interactions have been used to control the growth and microstructure of films used in a variety of applications including nonlinear optics, sensors, and transistors.² Halogen bonding (XB) is an intermolecular interaction involving a halogen atom (a Lewis acid) and a neutral or anionic Lewis base.³ XB plays an important role in natural systems⁴ and has been used for crystal engineering, liquid crystals, and template synthesis.⁵ Interestingly, XB exhibits characteristics similar to HB in directionality and strength; however, actual studies on these issues are far more rare.⁶ Because of these similarities, an intriguing question is whether molecules with XB functionalities (e.g. **1**, **2**) also enable the fabrication of thin films exhibiting well-defined microstructural characteristics.

Here we report the growth of highly crystalline halogen-bonded thin films grown by physical vapor deposition (PVD) on silicon substrates. Moreover, we demonstrate that the combination of substrate surface chemical functionalization with a monolayer of $\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{CN}$ (**3**) and the XB compound molecular structure plays a major role in determining the film's morphology and microstructure. Compound **3** was selected because of the strong interaction between the CN group and Lewis base moieties of XB molecules.⁷ Stilbazoles **1**⁸ and **2** are ideal molecular candidates owing to the (i) presence of both XB donor and acceptor functionalities, resulting in the formation of unimolecular halogen-bonded networks by a one-step deposition process, (ii) high thermal stability, and (iii) excellent volatility, a prerequisite for a reliable PVD process.



The syntheses of **2** is reported in the Supporting Information. Single-crystal analysis of compound **1** reveals the presence of a helical XB motif,⁸ whereas the molecular packing of the *N*-oxide derivative **2** consists of a strikingly different layered motif with an interlayer distance of 3.36 Å (Figure 1). Interestingly, the network of compound **2** consists of two different XB interactions. The first involves one of the two iodine atoms with the *N*-oxide moiety ($d = 2.82$ Å, $\theta = 173.9^\circ$). This moiety is also in short contact with a second iodine atom of an adjacent molecule ($d = 3.75$ Å, $\theta_1 = 102.4^\circ$, $\theta_2 = 171.9^\circ$),

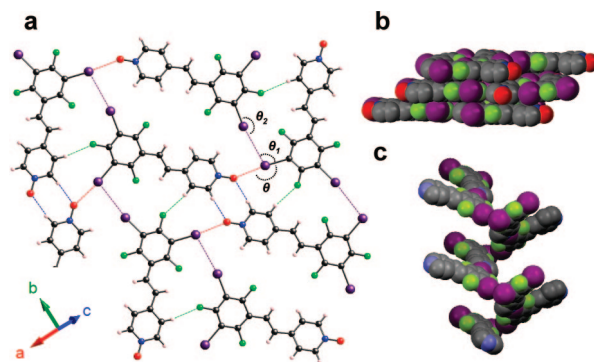


Figure 1. (a) One-dimensional (1D) crystal packing of compound **2** showing short intermolecular contacts as dashed lines: red, O...I; purple, I...I; blue, O...H-C; green, F...H-C. (b) Three-dimensional packing of compound **2** showing the layered structure. (c) Helical structure of compound **1**.⁸ Hydrogen atoms are omitted for (b, c).

which is aligned in the same plane. In addition, there are also relatively short NO...H-C contacts ($d = 2.37$ Å, $\theta = 169.8^\circ$). Introducing the *N*-oxide group results in drastic changes in the molecular packing; however, in both cases, a halogen-bonded network is formed.

Differential scanning calorimetry (DSC) of compounds **1** and **2** reveals no thermal transitions before melting, which occurs at 190 and 210 °C, respectively. Thermogravimetric analysis (TGA) reveals efficient sublimation, demonstrating the volatility and thermal robustness necessary for vacuum PVD. Thin films of compounds **1** and **2** (10 and 100 nm thick) were grown by PVD on bare silicon and silicon substrates functionalized with a **3**-based monolayer. The substrates were maintained at room temperature during the growth process. ¹H NMR analysis of the PVD-deposited films did not show evidence of decomposition of compounds **1** and **2**. The XB films were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD).

AFM images reveal that the film morphology of compound **1** consists of uniform grains regardless of the substrate surface (Figures 2a,b and S2). In contrast, the morphology of the assemblies grown from the *N*-oxide derivative (**2**) depends on the substrate surface chemical properties. Densely packed grains (height = 30–60 nm) are observed on bare silicon substrates (Figure 2c), whereas uniformly distributed islands (height = 20–35 nm) are formed on **3**-functionalized substrate monolayers (Figure 2d). The root-mean-square (rms) roughness of the areas between the islands (~ 0.2 nm) corresponds to the roughness of the **3**-based monolayers. Clearly, the *N*-oxide moiety of compound **2** plays a dominant structural role in controlling both the packing of the single crystals grown from solution and the morphology of the thin films. The interfacial interactions of compound **2** with the substrate surface are apparently strong enough to govern the growth mode of the entire assembly.

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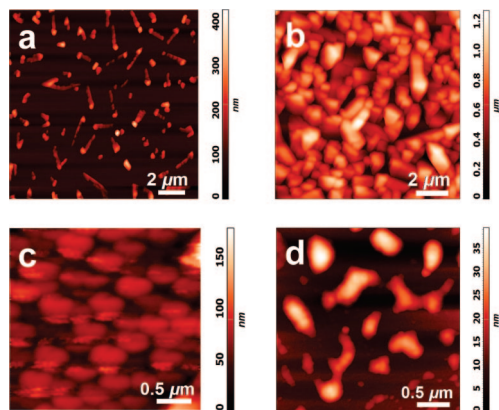


Figure 2. AFM images of 1- and 2-based films. (a, b) Compound 1 deposited on bare silicon (10 and 100 nm, respectively); (c, d) compound 2 deposited on bare silicon (10 nm) and on silicon substrates functionalized with a 3-based monolayer (10 nm), respectively.

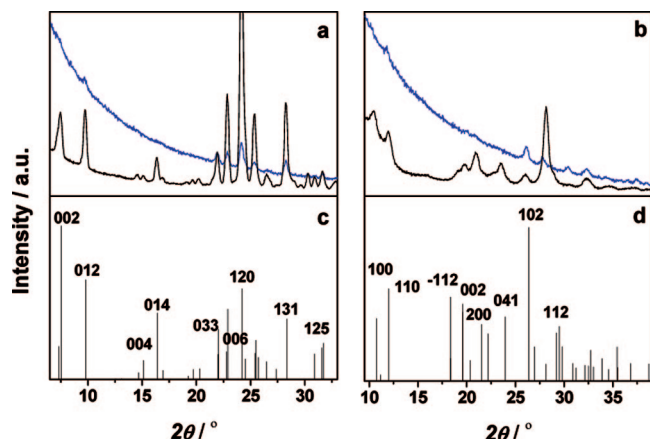


Figure 3. Experimental and simulated X-ray diffraction patterns of compounds 1 and 2. (a) Compound 1 on a silicon substrate modified with a 3-based monolayer (10 nm, blue) and on bare silicon (100 nm, black). (b) Compound 2 on a silicon substrate modified with a 3-based monolayer (10 nm, blue) and on bare silicon (100 nm, black). (c, d) Simulated XRD powder patterns with selected reflections labeled for compounds 1 and 2, respectively.

XRD measurements of the XB films show strong diffraction patterns, demonstrating the film's polycrystalline nature (Figures 3, S3, and S4). These films are far more textured than PVD grown films based on hydrogen bonding.^{2b} These experiments were carried out in two reflection modes for 100 nm thick films: (i) specular diffraction, θ – 2θ scans, which probe the crystallographic planes parallel to the plane of the substrate and (ii) asymmetric, 2θ , scans (incident angle 2°) that provide information independently of the crystallite preferred orientation. The 10 nm thick films were scanned in the 2θ mode. The XRD patterns indicate that the assemblies grown on different interfaces have similar crystalline phases—no preferred orientation of crystallites was observed. The XRD signals of the 1-based assemblies grown on bare silicon and those grown on 3-based monolayers on silicon substrates match well with the single-crystal lattice. The intensity of the set of peaks increases with increasing film thickness (from 10 to 100 nm, Figure 3), indicating that the structural order remains unchanged during the film growth process. The simulated powder pattern was used to assign the observed reflections (Figure 3c,d). The microstructures of the 1-based films and the single crystal grown from solution are identical.⁸ In contrast, the polycrystalline assemblies of compound 2 are different from the single-crystal structure. Several reflections are significantly shifted in comparison with the simulated powder pattern, demonstrating that 2–substrate surface interactions

are sufficient to vary the solid-state structure. Surprisingly, this result is independent of the Si surface chemistry.

In conclusion, the crystalline assemblies of 1 and 2, fabricated by PVD, exhibit controllable film morphologies. In particular, the surface morphology of 2-based assemblies can be varied from elongated features, cone-shaped grains, and interconnected islands to relatively large grains. Crystal growth morphology and molecular-based thin film formation guided by monolayer-based interfaces is of major interest.⁹ On the other hand, the corresponding film microstructures are independent of the substrate surface chemistry. This is very surprising for an organic thin film.² The molecular packing of 1-based assemblies is identical to solution grown crystals, whereas the thin films of compound 2 consist of a different polycrystalline structure. Apparently, introduction of an *N*-oxide moiety results in a looser crystal packing, which varies upon interaction with the substrate surface. However, in both cases, film XRD experiments demonstrate that the solid-state structure is independent of the substrate surface chemical functionalization. Since PVD is an established method for forming high-quality molecular-based electronic materials,¹⁰ we believe that halogen-bonded thin films may evolve into high-quality functional materials necessary for the development of new organic optoelectronic devices.^{2,11}

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Supporting Information Available: Experimental details for the formation of compound 2, PVD experiments with compounds 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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