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Complete List of Authors:	Gujral, Ankit; University of Wisconsin-Madison, Chemistry Gomez, Jaritza; University of Wisconsin-Madison, Chemistry Ruan, Shigang; University of Wisconsin-Madison, Department of Chemistry Toney, Michael; Stanford Synchrotron Radiation Laboratory, SLAC National Accelerator Laboratory Bock, Harald; CNRS-University of Bordeaux, Centre de Recherche Paul Pascal Yu, Lian; University of Wisconsin-Madison, School of Pharmacy Ediger, Mark; University of Wisconsin-Madison, Chemistry

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Vapor-deposited glasses with long-range columnar liquid crystalline order

Ankit Gujral¹, Jaritza Gómez¹, Shigang Ruan¹, Michael F. Toney², Harald Bock³, Lian Yu⁴, M.D. Ediger^{1*}

1. Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States

2. Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

3. Centre de Recherche Paul Pascal, Université de Bordeaux & CNRS, 33600 Pessac, France

4. School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States

ABSTRACT: Anisotropic molecular packing, particularly in highly ordered liquid-crystalline arrangements, has the potential for optimizing performance in organic electronic and optoelectronic applications. Here we show that physical vapor deposition can be used to prepare highly organized glassy solids of discotic liquid-crystalline systems. Using grazing incidence X-ray scattering, atomic force microscopy and UV/Vis spectroscopy, we compare three systems: a rectangular columnar liquid crystal, a hexagonal columnar liquid crystal and a non-mesogen. The packing motifs accessible by vapor deposition are highly organized for the liquid crystalline systems with columns propagating either in-plane or out-of-plane depending upon the substrate temperature during deposition. The structures formed at a given substrate temperature can be understood as resulting from partial equilibration toward the structure of the equilibrium liquid crystal surface during the deposition process.

INTRODUCTION

One of the central challenges in materials science is the control of molecular organization in solids. The ability to control molecular packing is required for the development of many technologically important fields. Among these fields are organic electronics and optoelectronics where molecular-scale packing modifications are being explored to engineer better devices.¹ Organic light emitting diodes (OLEDs), for instance, exhibit better outcoupling when emitter molecules are oriented in the solid matrix with their transition dipoles lying in-plane such that they emit preferentially perpendicular to the device face.² Microstructures with enhanced π -orbital overlap may also exhibit better charge carrier mobility in molecular systems;^{3,4} many such structures have anisotropic molecular packing arrangements. Preparation routes that lead to optimized microstructures have been investigated for small molecule and polymeric organic systems, a few of which are summarized here. Solution-shearing has been used to prepare anisotropic structures that lead to enhanced charge carrier mobility.⁵ Lattice strain, in combination with solution shearing, has been used to further increase orbital overlap between component molecules, thereby further enhancing mobility.⁶ Films prepared in the presence of external fields can also exhibit anisotropic packing and improved performance.^{7,8}

Liquid crystalline systems have been exploited for organic electronic applications as a result of their propensity to self-assemble into highly ordered, anisotropic struc-

tures.⁹⁻¹¹ Columnar liquid crystalline systems, in particular, are ideal candidates for organic semiconducting devices as they self-assemble into columnar superstructures governed, in part, by molecular cores rich in π -electrons.¹² The cores can form highly conjugated structures within the columns that exhibit high charge carrier mobility. However, the preparation of highly organized films of columnar liquid crystalline moieties has thus far required a thermal annealing process, sometimes on chemically altered substrates, to achieve the correct molecular packing structures.¹³ For instance, a sacrificial layer is required to induce face-on packing in certain discotic systems.¹⁴ While thermal annealing and chemically-tailored substrates may allow a desired structure to be achieved, these processing steps may also have deleterious effects on the performance of devices.

Physical vapor deposition, a method used in the industrial manufacture of OLEDs,¹⁵ can be used to control molecular organization in glassy solids by controlling deposition conditions, even for molecules without liquid crystalline phases.^{16,17} The structures prepared are trapped as non-equilibrium solids that are independent of underlying substrate chemistry; anisotropic structures can be achieved without subsequent annealing. Vapor-deposited glasses of non-liquid crystal systems show subtle structural and optical anisotropy (compared with liquid crystalline structures) but have, nonetheless, exhibited enhanced charge carrier mobility.³ Tunability of structure of vapor-deposited glasses of non-liquid crystal formers has

also been shown for a large number of systems, with structure controlled by the substrate temperature during deposition ($T_{\text{substrate}}$).^{16,18,19}

Combining vapor deposition as a route to anisotropic structures with the self-assembly of liquid crystals has recently been shown in one case to prepare films with highly organized and widely tunable structures.^{20,21} The structural anisotropy accessible by vapor deposition was investigated in itraconazole, a rod-shaped mesogen which enters the smectic phase (forming molecular layers) just above the glass transition temperature, T_g . The vapor-deposited structures varied from molecules laying almost exclusively in-plane (on average, 76° from substrate normal) to molecules “standing up” with the molecular long axes nearly along the substrate normal (27° from the normal). The layer spacing for $T_{\text{substrate}} = T_g$ to $T_g - 20$ K tracked the average molecular tilt angle, with higher tilts corresponding to smaller spacing, trapping the film into smectic-like packing arrangements not accessible in equilibrium, while below $T_g - 20$ K the molecules lie almost entirely in-plane. Some of the structures accessed by vapor deposition were more ordered than those prepared by extended thermal annealing of the same material.²⁰ Applying this approach to discotic liquid crystalline systems may provide access to highly tunable columnar structures, with columns propagating either in the plane of the substrate (useful, for instance, in field effect transistors) or out-of-plane (useful in photovoltaics). Important precedents exist for vapor deposition of discotic liquid crystals. Of particular relevance to the current work is a study by Eccher et al.²² which showed that vapor-deposited films of a discotic liquid crystal exhibited higher columnar order when compared with a spin-coated film of the same material. This led to higher charge carrier mobility in the vapor-deposited film. However, the range of possible structures that can be achieved by vapor deposition has not been investigated for any discotic system.

Here we investigate properties of films prepared by physical vapor deposition of three disc-shaped molecules (as shown in Figure 1): 2,6,10-triethoxycarbonyltriphenylene (a rectangular columnar mesogen, hereafter called triphenylene-ester), 1,16-di(methoxycarbonyl)-6,7,12,13-tetra(ethoxycarbonyl)phenanthro[ghi-1,2,3,4]perylene (a hexagonal columnar mesogen, hereafter called phenanthroperylene-ester) and m-MTDATA (4,4',4''-tris[phenyl(m-tolyl)amino]triphenylamine, a non-mesogen). The films were deposited over a range of substrate temperatures ranging from $\sim 0.75 T_g$ to $0.99 T_g$. We characterized molecular packing in the films as a function of $T_{\text{substrate}}$ by grazing incidence wide angle X-ray scattering (GIWAXS). Films prepared at $T_{\text{substrate}} \sim T_g$ exhibited in-plane columnar structures with long range order for the two mesogens, while an isotropic disordered structure was observed for the non-mesogen. Films prepared at low $T_{\text{substrate}}$ exhibited face-on packing arrangements for all three systems, with out-of-plane columnar structures for one the mesogens. Atomic force microscopy (AFM) was used to determine surface morphology of the various films, and domain-like structures were found in the highly-organized films. UV/Visible spectroscopy (UV/Vis) was

used to show that the local electronic environment in the highly-ordered films prepared by vapor deposition is similar to that in the equilibrium liquid crystal. We investigated the thermodynamic state of the films by conducting temperature annealing experiments; the as-deposited films are best described as glassy materials.

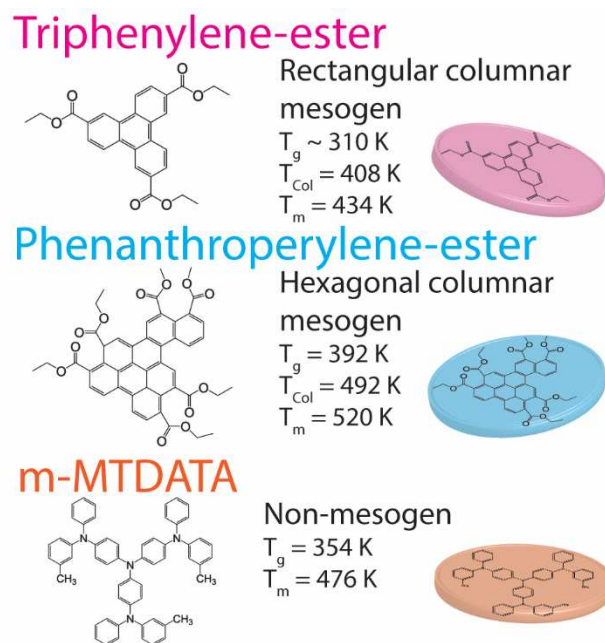


Figure 1. The three systems investigated, with molecular structures and transition temperatures. Also shown is a color-coded schematic that will be used to describe the systems in later figures.

These results suggest that vapor deposition of discotic liquid crystals may be generally useful for preparation of highly organized films and that the substrate temperature during deposition will provide access to a wide range of packing arrangements. The structures observed in this work can be explained by a mechanism invoking a combination of two factors: the tendency to self-assemble at the free surface of the equilibrium liquid^{16,23–25}, and enhanced mobility at the free-surface of glasses^{26,27}. The generality of this mechanism suggests that these results may be extended to other columnar liquid crystal systems, and other classes of liquid crystals, that have a propensity to self-assemble into highly organized structures at vacuum interfaces.

EXPERIMENTAL METHODS

Materials. m-MTDATA was purchased from Sigma-Aldrich (>99% pure) and used as-received. m-MTDATA does not exhibit any liquid crystalline phases. It has a melting point of $T_m = 476$ K and a glass transition temperature of $T_g = 354$ K. The triphenylene-ester was synthesized as described in ref²⁸. It exhibits a columnar phase below 408 K and its crystalline solid has a melting temperature $T_m = 434$ K. We estimate that $T_g \sim 310$ K based on

in-situ thin film transformation experiments. The phenanthroperylene-ester was synthesized as described in ref.²⁹. It exhibits a columnar hexagonal phase below 492 K. Its crystalline solid undergoes a melting transition at $T_m = 520$ K. It undergoes a glass transition at $T_g = 392$ K.²⁹

Vapor deposition. Glasses of the three systems were prepared by physical vapor deposition onto either a silicon <100> substrate with native oxide or a fused silica substrate. The deposition rate was maintained at 0.2 ± 0.02 nm/s in a vacuum chamber (base pressure $\sim 10^{-7}$ torr), monitored using a Quartz Crystal Microbalance (Sycon). The substrates were held on copper blocks that were maintained at the desired substrate temperature using a LakeShore 336 PID controller (LakeShore Cryotronics, Inc.) paired with resistive cartridge heaters (Southwest Heater Corp.) and platinum resistive temperature detectors (Omega Engineering., Spectris PLC). Thermal paste (Apiezon N or H, for low or high temperatures, respectively) was smeared between the substrates and the copper to maintain thermal contact in the vacuum environment. Roughly 150 nm films were deposited on silicon substrates for grazing incidence wide-angle X-ray scattering (GIWAXS) and for the Atomic Force Microscopy (AFM) measurements. For UV/Visible absorption spectroscopy (UV/Vis), 90–120 nm films were prepared on fused silica substrates.

GIWAXS. GIWAXS measurements were conducted at beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). The wavelength of the incident beam was 0.973 Å, with a detector resolution of 0.002 Å⁻¹/pixel (detector distance = 300 mm). The incident angle was set to 0.14° to assure that the scattering occurred in the bulk of the film and exposure was typically less than 120 seconds. The data was processed with the SSRL-developed WxDiff software package. Following the protocol outlined in Baker et al.,³⁰ the diffraction patterns were corrected for polarization of the beam and χ -corrected to obtain accurate reciprocal space maps. GIWAXS measurements were performed at room temperature except as noted.

AFM. Atomic force microscopy (AFM) measurements were conducted on a Bruker MultiMode 8 AFM using ScanAsyst PeakForce Tapping mode. The measurements were conducted at room temperature.

UV/Vis. UV/Visible absorption spectra were collected on a JA Woollam M-2000 Variable Angle Spectroscopic Ellipsometer with a wavelength range of 245 nm to 1000 nm. The samples were mounted and measured in transmission geometry at normal incidence. A spot size of roughly 2 mm was used. These samples were also analyzed using X-ray diffraction, with the results indicating no significant difference in structure for films prepared on fused silica and on silicon.

RESULTS

Molecular packing. Figure 2 shows two-dimensional (2D) grazing incidence wide angle X-ray scattering (GIWAXS) patterns for vapor-deposited films of the triphenylene-ester, the phenanthroperylene-ester and m-MTDATA; scattering intensity is illustrated in a linear

color-scheme from red to blue representing high to low intensity): Also shown are schematic illustrations describing molecular packing motifs that are consistent with the GIWAXS patterns, as we discuss below. For each system, two GIWAXS patterns are shown, one for a sample deposited at roughly $T_{\text{substrate}} \sim 0.75T_g$ (top pattern within each panel) and the other for $T_{\text{substrate}} \sim T_g$ (bottom pattern within each panel); the absolute $T_{\text{substrate}}$ is indicated. The GIWAXS measurements were all made at room temperature for this section of the paper.

As shown in Figure 2, films prepared at low $T_{\text{substrate}}$ for all three systems exhibit a roughly face-on molecular packing motif, while at $T_{\text{substrate}} \sim T_g$ quite distinct packing structures are attained by the three systems. To facilitate our discussion, we begin with a brief description of the 2D scattering patterns. The axes of the 2D GIWAXS patterns represent components of the scattering wavevector, q (reported in Å⁻¹), defined as $q = 4\pi \sin \theta / \lambda$, where θ is $1/2$ the scattering angle and λ is the wavelength of the X-ray beam. q_{xy} and q_z represent the in-plane and out-of-plane wavevectors, respectively. For our samples, we did not observe a significant change in the scattering pattern upon rotating the films in the xy -plane (substrate plane). Thus, q_x and q_y are equivalent and the films are in-plane isotropic on the length-scale probed by the GIWAXS experiments (roughly 1 mm^2); The scattering position of the bright peaks in the pattern correspond inversely to real-space periodicity of the structures, d , by the relationship $d = 2\pi/q$. Scattering features along q_{xy} (horizontal axis) correspond to ordering in the plane of the substrate while features appearing along q_z (vertical axis) correspond to ordering out-of-plane.

We will begin our analysis with the triphenylene-ester, a columnar rectangular mesogen, focusing on the data in the top panel (pink) in Figure 2. Scattering patterns from two glasses are displayed describing the two representative structures accessible by vapor-depositing at low and high $T_{\text{substrate}}$ for the system. Even though some of these scattering patterns indicate high levels of liquid crystal-like order, they are best described as “glasses” as we discuss below. For the pattern obtained from the glass prepared at $T_{\text{substrate}} = 240$ K ($\sim 0.77T_g$), a broad diffraction peak can be seen at $q_z \sim 1.75$ Å⁻¹, corresponding to a real-space 3.7 Å periodic structure propagating out-of-plane, that can be inferred to be a π - π stacking structure. A diffraction peak appearing in-plane at $q_{xy} \sim 0.5$ Å⁻¹ indicates in-plane periodicity corresponding to roughly 13 Å, approximately a molecular diameter. These two features combined show a columnar structure with columns propagating out-of-plane as shown in the schematic alongside the pattern. There is some disorder within the columns reflected in the breadth of the peak at $q_z \sim 1.75$ Å⁻¹.

By comparison, the film prepared at $T_{\text{substrate}} = 295$ K ($T_{\text{substrate}} \sim T_g$), is highly ordered with columns propagating in-plane. The in-plane columnar structures are evidenced from the in-plane diffraction peak at $q_{xy} \sim 1.8$ Å⁻¹ (notice this peak is not detectable along q_z). This peak corresponds to a real-space periodic structure of 3.5 Å, indicating a more tightly packed π - π interaction between molecules within the same column than in the sample

prepared at lower $T_{\text{substrate}}$. The sharpness of the peak at $1.8 \text{ \AA}^{-1}$ (azimuthally as well as along q_{xy}) relative to the low deposition temperature film indicates that the columns formed in this film are much more highly ordered and oriented. The columns themselves form a rectangular (distorted hexagonal) structure, as inferred from the rectangular grid-like pattern, with columns packing farther apart out-of-plane ($d_{\text{out-of-plane}} = 13.6 \text{ \AA}$) than in-plane ($d_{\text{in-plane}} = 11.5 \text{ \AA}$), as shown in the schematic ($a = 13.6 \text{ \AA}$, $b = 11.5 \text{ \AA}$, $c = 3.5 \text{ \AA}$). This structure in the high $T_{\text{substrate}}$ film is similar to planar aligned equilibrium liquid films of columnar liquid crystal structures (with columns parallel to substrate).³¹ As the GIWAXS experiments indicate that the film is macroscopically isotropic in the plane of the substrate, we infer that there must be an isotropic distribution of in-plane columnar structures in domain-like formations. The peak at $q_{xy} \sim 1.8 \text{ \AA}^{-1}$ results from the subset of structures with columns perpendicular to the beam while the rectangular grid-like pattern results from the subset of columns that propagate along the beam. We discuss the likely size of these domains below. GIWAXS patterns obtained for intermediate values of $T_{\text{substrate}}$ for this system show structures similar to the two displayed in Figures 2, with a transition between the two structures occurring over about 10 K in $T_{\text{substrate}}$ near 265 K. The observation that this transition occurs about 50 K below T_g ($\sim 310 \text{ K}$) is highly relevant for understanding the mechanism by which vapor deposition prepares these ordered structures.

Vapor-deposited films of the phenanthroperylene-ester, a hexagonal columnar mesogen, also exhibit two representative structures, as shown in the second (blue) panel of Figure 2. The film deposited at low $T_{\text{substrate}}$ exhibits a preferred face-on packing arrangement with a broad diffraction peak (with scattering spread radially) centered around $q_z \sim 1.75 \text{ \AA}^{-1}$; this broad orientational pattern indicates a packing arrangement with a wide distribution of out-of-plane periodic structures. This peak corresponds to a $3.6 \text{ \AA}$ disordered out-of-plane packing structure. There is another highly textured ring diffracting most strongly in-plane at $q_{xy} \sim 0.45 \text{ \AA}^{-1}$ (or, $d \sim 13.9 \text{ \AA}$), corresponding to a molecular diameter indicating nearest-neighbor order predominantly orthogonal to the π - π interaction direction. Films deposited at high $T_{\text{substrate}}$ (near T_g) are highly ordered. There is a fairly sharp feature indicative of π - π stacking in-plane at $q_{xy} \sim 1.8 \text{ \AA}^{-1}$ ($d = 3.5 \text{ \AA}$), and very sharp peaks at $q_z \sim 0.45 \text{ \AA}^{-1}$ as well as azimuthally along a 60-degree angle from q_z , showing a hexagonal packing superstructure between columns ($a = 13.9 \text{ \AA}$; $c = 3.5 \text{ \AA}$). This is shown schematically alongside the scattering pattern and is similar to the structure of an aligned equilibrium film of the phenanthroperylene-ester, as shown below. As in the case of the triphenylene-ester system, the schematic for

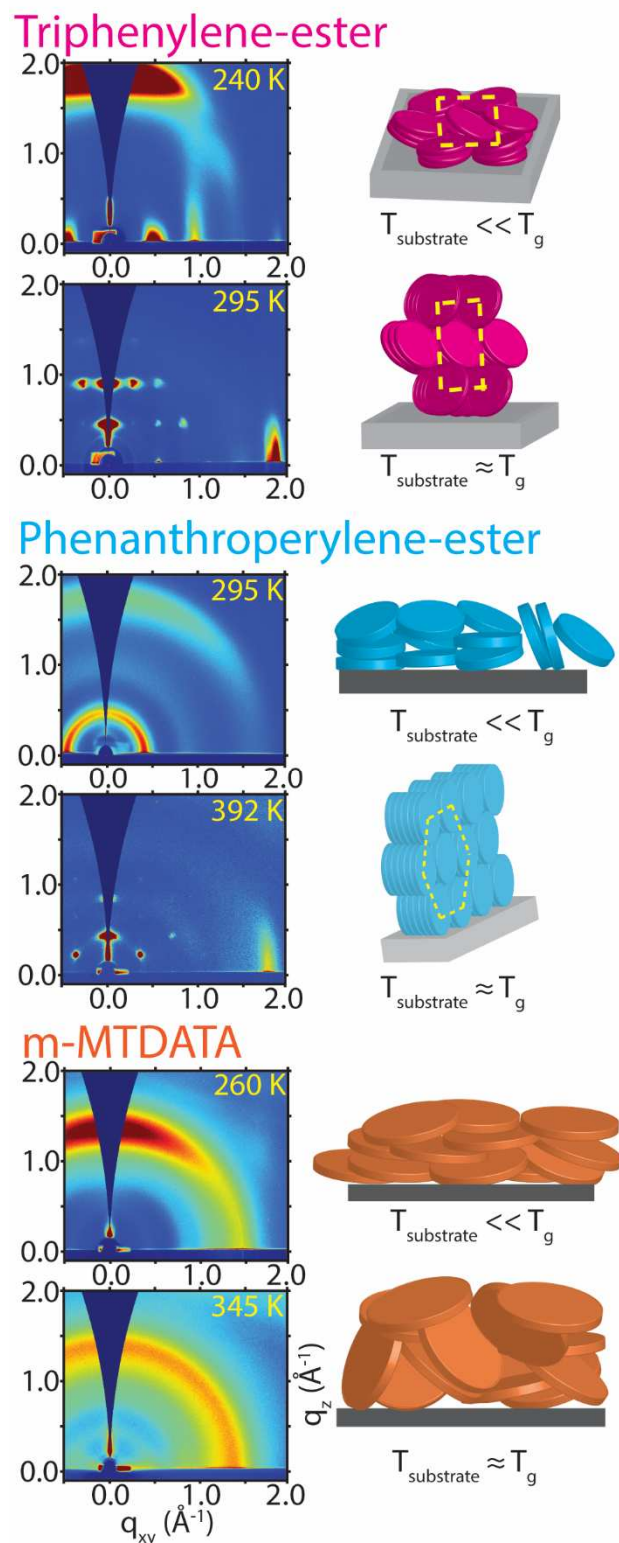


Figure 2. 2D GIWAXS patterns obtained from vapor-deposited films ($\sim 150 \text{ nm}$ thick) of three systems, with schematics describing molecular packing. For each system, data is shown for glasses prepared at $T_{\text{substrate}} \sim 0.75T_g$ (upper panel) and $T_{\text{substrate}} \sim T_g$ (lower panel). The scattering patterns are symmetric about $q_{xy}=0$; part of the negative q_{xy} data is shown to more clearly reveal this scattering symmetry. In the schematics, each disk represents one molecule.

the high temperature sample is representative of one domain-like structure. While film structures accessible in the phenanthroperylene-ester and the triphenylene-ester share some common phenomenology, the phenanthroperylene-ester films show a more continuous transition in structure as $T_{\text{substrate}}$ is varied. At intermediate substrate temperatures, disordered versions of the high temperature hexagonal packing motif can be accessed. These structures will be discussed below and their scattering patterns can be found in Figure 5.

Unlike the two systems discussed above, m-MTDATA (Figure 2 third panel, orange) is a non-mesogen. Films prepared at low $T_{\text{substrate}}$ exhibit a slightly face-on packing motif as inferred from the anisotropy in the amorphous halo at $q \sim 1.4 \text{ \AA}^{-1}$ in the top pattern, indicative of some preference for face-on packing with π stacking out-of-plane. A film deposited at $T_{\text{substrate}} \sim T_g$, on the other hand is isotropic and disordered, similar to the structure expected for the equilibrium supercooled liquid of m-MTDATA. Structures trapped into films at intermediate values of $T_{\text{substrate}}$ monotonically become more ordered with decreasing $T_{\text{substrate}}$. This observation is in qualitative agreement with optical measurements¹⁹ of the molecular orientation of m-MTDATA which showed that the molecules go from isotropically organized to preferentially laying in-plane from high $T_{\text{substrate}}$ to low $T_{\text{substrate}}$.

Film morphology. Film morphology is important when considering these materials for applications and it provides further insight into the structure and organization of the films that cannot be provided by GIWAXS. We used atomic force microscopy (AFM) to investigate the surface morphology of vapor-deposited films of the three systems. Figure 3 shows AFM micrographs from low $T_{\text{substrate}}$ and high $T_{\text{substrate}}$ films of the triphenylene-ester, the phenanthroperylene-ester and m-MTDATA. All AFM measurements were performed at room temperature. As discussed above, the highly-ordered films prepared from columnar liquid crystals at $T_{\text{substrate}} \sim T_g$ are expected to exhibit domain-like structures in the plane of the substrate. While the surface morphology may not necessarily reflect the bulk morphology, we argue below that the surface features provide a reasonable first approximation to the domain structure in the bulk.

For the triphenylene-ester, films prepared at low $T_{\text{substrate}}$ (left micrograph of top panel in Figure 3) are molecularly smooth ($R_q = 0.4 \text{ nm}$; where R_q is the root mean square average height deviation from the mean image plane). In contrast, the film prepared at high $T_{\text{substrate}}$ (right micrograph) for the same molecule exhibits domains a few 100 nm in size ($R_q = 3.0 \text{ nm}$). We interpret the domains observed at high $T_{\text{substrate}}$ as regions in which columnar structures propagate in a single direction. This is consistent with a rudimentary Scherrer analysis, based on the peak widths of the columnar scattering peaks ($\Delta q = 0.018 \text{ \AA}^{-1}$), indicating domains of at least 35 nm in the bulk. For films prepared at low $T_{\text{substrate}}$, the face-on packing inferred from the scattering pattern does not require the presence of in-plane domains and this is consistent with the smooth nature of the surface.

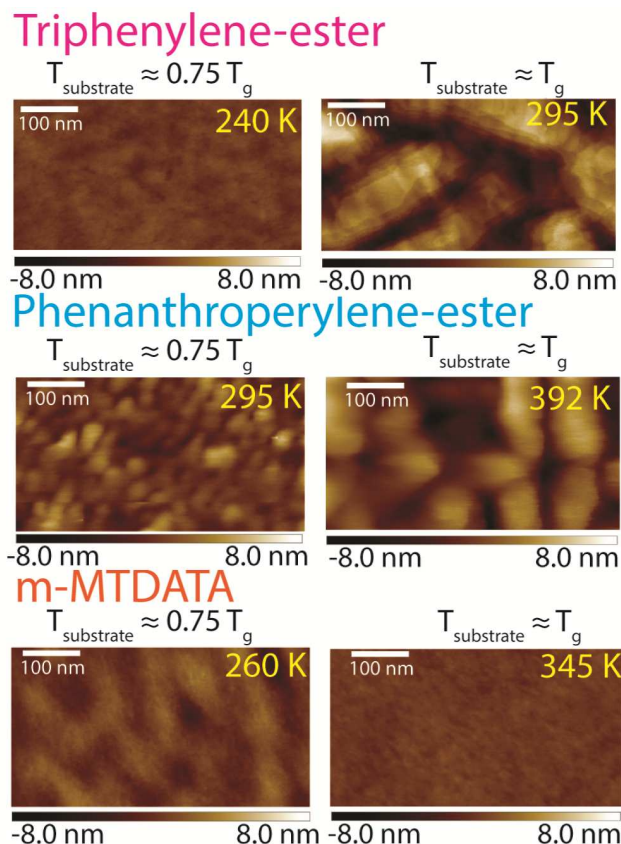


Figure 3. AFM micrographs for glasses vapor-deposited at $T_{\text{substrate}} \sim 0.75 T_g$ (left) and $T_{\text{substrate}} \sim T_g$ (right) for three systems. The height contrast color scale is kept constant at $\pm 8 \text{ nm}$ for all the micrographs. The two liquid crystal systems exhibit domain-like structures in the films deposited at $T_{\text{substrate}} \sim T_g$ (and the phenanthroperylene-ester shows domain-like structures also in the low $T_{\text{substrate}}$ films). The non-mesogen, m-MTDATA, on the other hand, forms molecularly smooth films across the $T_{\text{substrate}}$ regime investigated.

In vapor-deposited films of the phenanthroperylene-ester, domains are observed in the AFM images for films prepared at both low and high $T_{\text{substrate}}$. The domains get smaller as $T_{\text{substrate}}$ is lowered, ranging from a few 100 nm (with $R_q = 2.8 \text{ nm}$) for $T_{\text{substrate}} \sim T_g$ to tens of nm in size (with $R_q = 2.2 \text{ nm}$) for $T_{\text{substrate}} \sim 0.75 T_g$ films (AFM micrographs from intermediate substrate temperatures have been excluded for brevity). The domains in the films prepared at high $T_{\text{substrate}}$ are similar to those observed in the triphenylene-ester and we imagine that one domain corresponds to a region of uniform in-plane alignment for the superstructure shown in the schematic in Figure 2, with the domains randomly distributed in-plane on the larger length scale probed by GIWAXS. We interpret the domains observed for the phenanthroperylene-ester film prepared at low $T_{\text{substrate}}$ in light of the scattering pattern for this film in Figure 2. The $q \sim 0.45 \text{ \AA}^{-1}$ feature indicates the presence of somewhat disordered columns propagating along the surface normal. The domain sizes observed in the AFM are smaller for low $T_{\text{substrate}}$ films, consistent with the increased disorder.

Films of m-MTDATA are molecularly smooth ($R_{q,345 \text{ K}} = 0.6 \text{ nm}$; $R_{q,260 \text{ K}} = 1.1 \text{ nm}$), and exhibit no significant do-

main-like structures regardless of $T_{\text{substrate}}$. For the film prepared at $T_{\text{substrate}} \sim T_g$, this is in agreement with our expectation that this film is identical to a glass prepared by cooling the isotropic liquid. The film prepared at low $T_{\text{substrate}}$ is also highly disordered according to Figure 2, in comparison to films prepared from mesogens; domains would not seem to be required in such a disordered material.

Spectral shifts in vapor-deposited films. For many applications involving organic electronics and optoelectronics, the delocalization of electronic states within the material is highly relevant. Charge carrier mobility in organic materials is controlled by several factors,^{5,32–38} and large π -conjugation between molecules is of predominant importance in non-polymeric organic electronic materials.³⁹ To gain some insight into this, we compared UV/Visible absorption (UV/Vis) spectra for vapor-deposited glasses of the phenanthroperylene-ester deposited at two temperatures with a glass prepared by cooling the equilibrium liquid crystal state of this system.

Figure 4 shows the UV/Vis spectra as a function of wavelength for the three phenanthroperylene-ester films: a film deposited at $T_{\text{substrate}} = 295$ K, a film deposited at $T_{\text{substrate}} = 387$ K, and a film cooled to room temperature after extended annealing in the equilibrium liquid crystal phase. The position of absorption features in the UV/Vis spectra can be indicative of relative electron delocalization, with red-shifted features consistent with more delocalization in the system.^{40,41} We observe a roughly 6 nm red-shift associated with the highest wavelength (lowest energy) absorption (~ 460 nm) in the film deposited at $T_{\text{substrate}} = 387$ K when compared to the film deposited at $T_{\text{substrate}} = 295$ K. This is consistent with better π -conjugation in the film deposited at the higher temperature than in the lower temperature film although other factors can also influence the spectral shift. The interpretation of enhanced π -conjugation matches our expectation based upon Figure 2 in that the more ordered structure shows red-shifted absorption. Interestingly, when the film prepared at $T_{\text{substrate}} = 387$ K was annealed for one hour at $T_g + 10$ K, no peak shift was observed. This indicates that the local electronic environment is similar before and after annealing and that, at least on a local level, the extent of ordering in the $T_{\text{substrate}} \sim T_g$ vapor-deposited film is similar to that of the equilibrium liquid crystal. As a point of reference, the shift of the absorption of the lowest energy electronic state shown in Figure 4 is comparable to shifts in peak absorption between various crystal polymorphs of Alq_3 (aluminum tris(8-hydroxyquinoline)), with the red-shifted Alq_3 polymorph believed to exhibit greater π -conjugation between ligands.⁴² A larger, roughly 20 nm, shift is seen between an isotropic and nematic polymeric liquid crystal aligned with a polyimide-treated substrate and an external field.⁴¹

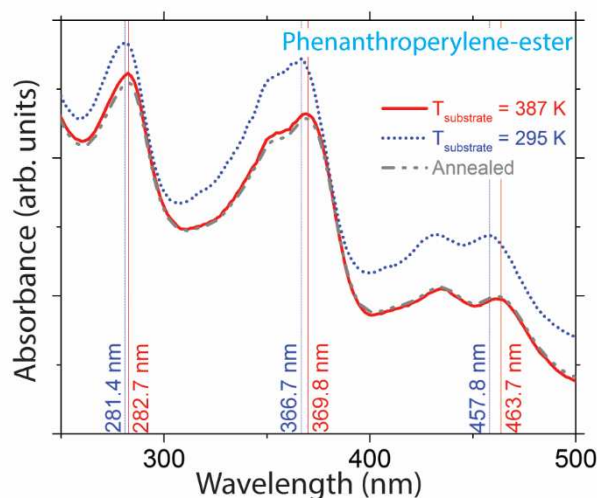


Figure 4. UV/Visible absorption spectra for three films of the phenanthroperylene-ester: a vapor-deposited film ($T_{\text{substrate}} = 295$ K = $0.75T_g$, blue dotted line), a highly-ordered vapor-deposited film ($T_{\text{substrate}} = 387$ K = $0.99T_g$, red solid line) and a film annealed at 402 K ($T_g + 10$ K) for an hour before cooling back to room temperature for the measurement (gray dashed line). Three peak positions are labeled with vertical lines to highlight the redshift observed for the highly-ordered vapor-deposited sample relative to the less ordered sample deposited at lower temperature.

As-deposited films are not three-dimensional crystalline solids. We begin by reviewing some important features of glasses formed from liquid crystals. While some liquid crystals undergo a first order transition to a 3D crystal upon cooling, others (including the phenanthroperylene ester²⁹) form a glass.^{10,21,43} This process is analogous to forming a glass by cooling an isotropic liquid. As the temperature decreases, the timescale for molecular motion slows. At T_g , the molecules can no longer rearrange to achieve equilibrium and a glass is formed.⁴⁴ For both isotropic liquids and liquid crystals, the glassy state is characterized by a smaller heat capacity relative to the fluid state and physical aging (enthalpy relaxation).^{10,43} While an isotropic liquid yields an isotropic glass upon cooling, the glass formed from a liquid crystal inherits the anisotropic structure of the liquid crystalline phase. Typically, when the glass of liquid crystal is heated, the fluid liquid crystalline phase is recovered.^{10,43}

We can use an annealing experiment to show that the vapor-deposited films are glassy solids as opposed to three-dimensional (3D) crystals. Figure 5 shows GIWAXS patterns obtained from three phenanthroperylene-ester films, before (left) and after (right) annealing above T_g . On the left, are patterns obtained from films prepared at $T_{\text{substrate}} = 295$ K, 335 K and 360 K ($0.75T_g$, $0.85T_g$ and $0.92T_g$). The patterns on the right were obtained from the same films after a 12 minute anneal at 402 K ($= T_g + 10$ K = $T_m - 118$ K). All the patterns shown here were obtained at room temperature; *in-situ* diffraction patterns obtained during annealing are shown in Supplementary Information. Upon annealing, all three films evolve to some extent towards a columnar hexagonal scattering pattern that we assign to the equilibrium liquid crystalline

phase;^{45–48} this scattering pattern is most clearly seen in the lower right image in Figure 5. Consistent with this interpretation, the lower right image only has peaks that can be attributed to the 2D columnar lattice and a broader peak associated with disk-to-disk π - π distance; this broader peak indicates disorder along the column direction and is expected for a liquid crystalline structure. Furthermore, mixed index peaks (arising from lattice planes intersecting the column direction) would be expected for a 3D crystal; the absence of such peaks supports the view that neither the as-deposited films nor the annealed films are 3D crystals. This conclusion is further supported by comparing the X-ray diffraction pattern of crystalline phenanthroperylene-ester with the vapor-deposited films, shown in the SI.

In Figure 5, the films deposited at $T_{\text{substrate}} = 335$ K and 360 K are initially disordered forms of the equilibrium edge-on columnar structure that become more ordered upon annealing. The evolution of the $T_{\text{substrate}} = 295$ K sample upon annealing is discussed below. *The observation that all three films evolve into the equilibrium liquid crystal when held 118 K below the melting temperature indicates that the as-deposited films are not crystalline.* On the contrary, if the as-deposited films were disordered crystals, T_g would be irrelevant and we would expect little structural evolution so far below T_m ; any changes that did occur would be expected to commence at a temperature unrelated to T_g and yield a 3D crystal rather than a liquid crystal.

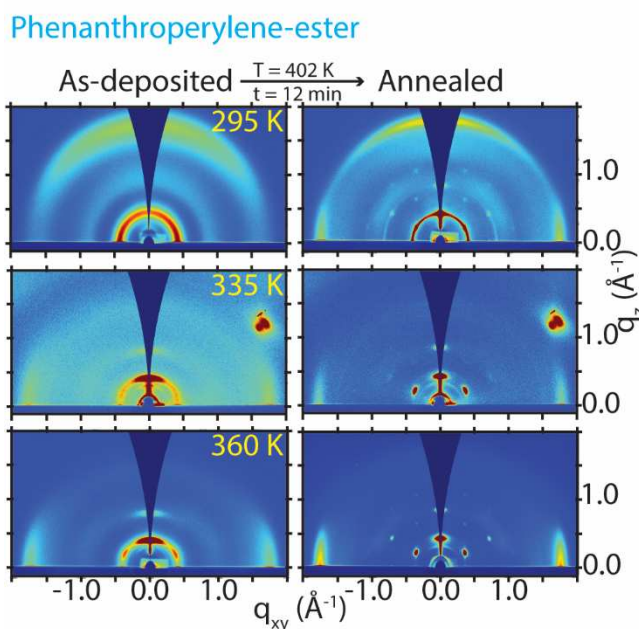


Figure 5. 2D GIWAXS patterns for three vapor-deposited films of the phenanthroperylene-ester before and after annealing at $T = 402$ K ($T_g + 10$ K) for 12 minutes, with $T_{\text{substrate}}$ values indicated. The left column shows patterns for the as-deposited glasses while the right column shows patterns after annealing. All the films evolve towards the hexagonal liquid crystal with homeotropic molecular alignment. In both patterns for the $T_{\text{substrate}} = 335$ K sample, the bright feature at $q_{xy} = 1.7$ and $q_z = 1.2$ $\text{\AA}^{-1}$ is diffuse scatter from the underlying

silicon substrate and not from the phenanthroperylene-ester film.

The structural evolution of the $T_{\text{substrate}} = 295$ K sample upon annealing is particularly interesting as it gives us a window into the transformation process. After the 12-minute anneal at 402 K, the film is only partially transformed into the preferred planar alignment. An extended anneal of 5 days at the same temperature completely transforms the film into a planar aligned liquid crystal. The GIWAXS patterns in the SI illustrate that this transformation begins at the free surface (vacuum interface) with the molecules anchoring edge-on (planar columnar alignment). During annealing, the bulk of the film initially perfects the pre-existing microstructure (as can be observed, for instance, by the sharpening of the out-of-plane peak at $q_z \sim 1.75$ $\text{\AA}^{-1}$ among other features); eventually the preferred planar column geometry propagates from the free surface through the bulk of the film.

DISCUSSION

The origin of structural anisotropy observed in vapor-deposited films. For each of the three systems investigated here, quite different structures can be prepared by physical vapor deposition, depending upon the choice of substrate temperature during deposition. A surface equilibration mechanism based on molecular dynamics simulations has been proposed to explain how non-mesogens form anisotropic glasses through the physical vapor deposition process.^{16,25} Very recent work has utilized this approach to understand the structures prepared by vapor deposition of a smectic mesogen.²⁰ In this section, we show that this mechanism can also account, at least qualitatively, for the structures observed here for columnar mesogens.

It has been shown that vapor deposition of organic molecules that are not mesogens can produce glasses with higher thermal stability and higher density than glasses of the same system quenched from a liquid;^{49,50} at a deposition rate of 0.2 nm/s, the largest effects are often observed for $T_{\text{substrate}} \sim 0.85T_g$. The development of these properties is attributed to high mobility near the free surface of the glass that allows molecules near the surface to partially equilibrate as they are being deposited onto the film. During the vapor deposition process, every molecule that lands on the film is, for a short time, part of the highly mobile surface before being buried by the next layers of molecules. During their short residence time at the free surface (~ 5 seconds for a typical deposition rate), molecules have enough mobility to find efficient packing arrangements. Further deposition traps these packing arrangements in the bulk material, resulting in high density and high thermal stability.

The structural anisotropy in vapor-deposited glasses can also be traced back to the enhanced surface mobility described above along with one additional feature: the preferred structural packing of the molecules at the free surface of the liquid. Molecular dynamics simulations of coarse-grained¹⁶ and atomistic^{19,25} non-liquid crystal form-

ing systems have provided the mechanism to explain anisotropy in vapor-deposited glasses. For example, liquid m-MTDATA was simulated and it was found that at the free surface of the equilibrium liquid, molecules tend to lie flat in the plane of the film, while deeper into the liquid the structure was isotropic. When m-MTDATA is deposited far below T_g ($T_{\text{substrate}} \sim 0.75T_g$, in Figure 2), the anisotropic structure that is preferred at the free surface is trapped into the bulk of the film. In contrast, when m-MTDATA is deposited at high $T_{\text{substrate}}$ (just below T_g), the mobility near the free surface propagates deep enough into the film that isotropic packing arrangements are trapped by subsequent deposition (as shown in Figure 2).

The surface equilibration mechanism can also be used to explain the structures prepared by vapor deposition of liquid crystals. Gujral et al. vapor-deposited a smectic liquid crystalline system, itraconazole,²⁰ finding that deposition near T_g resulted in a highly ordered glass with structure similar to a smectic monodomain. In smectic liquid crystals, the free surface structure in equilibrium involves homeotropic anchoring (where the molecular long axis is perpendicular to the vacuum interface) and smectic layers parallel to the interface.²⁴ When deposited near T_g , high mobility allows each layer to form this equilibrium structure and further deposition traps this structure into the glass.

For columnar systems, the vacuum interface generally induces edge-on molecular alignment (i.e., columns propagating in-plane).^{31,51} Thus, the edge-on molecular alignment motif will be assembled during the deposition process if surface mobility is sufficient. For depositions with $T_{\text{substrate}} \sim T_g$, this leads to the highly-ordered structures shown in Figure 2 for the two mesogens in this study. As each new layer is deposited, the molecules align edge-on along the free surface, with the same director and in registry with the underlying layer, as they would in an equilibrium film, before being trapped in this arrangement by oncoming molecules. This explains why the observed superstructures mimic the equilibrium hexagonal and rectangular columnar structures for the phenanthroperylene-ester and the triphenylene-ester, respectively. Since in-plane structures are being formed simultaneously on all parts of the film and there is no driving force for macroscopic alignment, there should be a domain structure with a uniform distribution of in-plane directors, consistent with our observations. This highly ordered structure is observed when deposition occurs considerably below T_g (down to $T_g - 50$ K for the triphenylene system) and is an indication that surface mobility is much higher than bulk mobility, as observed previously for glasses of organic molecules that are not mesogens.²⁶

For deposition of the columnar liquid crystal systems at $T_{\text{substrate}} \sim 0.75T_g$, surface mobility is lower and molecules at the free surface are unable to rearrange into the preferred edge-on molecular alignment before being buried by the next layer of molecules. In this temperature regime, we infer that the molecules deposited on the film initially tend to lie flat in the plane, and are trapped in this motif upon further deposition; this is consistent with observations for low temperature depositions of non-

mesogens.^{16,19} For both liquid crystalline systems in Figure 2, there is evidence for preferential π - π stacking out-of-plane with columnar structures propagating out-of-plane. For the low temperature depositions, the triphenylene-ester films are more highly ordered than the phenanthroperylene-ester films. We conjecture that this may be due to the high symmetry of the triphenylene-ester molecule; minimal molecular rearrangement would be required to form the in-plane rectangular structures observed in these films.

Previous studies involving columnar liquid crystalline systems have shown there is an order-induced enhancement in charge carrier mobility.⁵² Eccher et al., for instance, showed that vapor depositing a discotic derivative of benzo[ghi]perylene led to higher charge carrier mobility than a spin-coated film of the same material, but still higher charge mobility was observed in a highly annealed sample.²² In that work, the deposited films were prepared by deposition onto a substrate at ambient conditions. We interpret this result to indicate that deposition at a low substrate temperature resulted in a relatively disordered film that, upon annealing, increased in order and electrical performance. In the present work, we have shown that by careful choice of substrate temperature during deposition, the as-deposited film does not need to be annealed to prepare a highly-ordered film. Moreover, the substrate temperature can also determine if the ordered structures are packed edge-on or face-on.

Based upon the results presented here for columnar mesogens and those presented previously for a smectic liquid crystal,^{20,21} we suggest that vapor deposition can be used generically with various liquid crystalline systems to prepare highly ordered and highly tunable packing motifs in glassy films. In this study we confirmed that the structures of the as-deposited films are identical for deposition onto fused silica and silicon, it has been shown elsewhere that the as-deposited structures are independent of a wider range of underlying substrates.²¹ Similarly, preliminary data on thicker films of the columnar systems (300 nm) indicates that the structures of the as-deposited films are independent of thickness; for other vapor-deposited systems, this has been shown for a much wider range of thicknesses and systems, from 20 nm⁵³ to microns²⁰. These findings are consistent with the surface equilibration mechanism since the structure trapped in the solid films is directed by the free surface (and not the substrate).

Potential applications. Manipulating organization and structure in organic solids is a crucial step towards engineering better films for organic electronic and optoelectronic devices. Liquid crystalline moieties have been explored for this purpose and glasses prepared from liquid crystals have been investigated for a variety of applications from thin film transistors to polarizers and optical notch filters.¹⁰ In these studies, however, the ordered layers were prepared by thermal annealing and then quenched to attain the required morphology.

In comparison to thermal annealing, vapor deposition presents a number of potential advantages as a means to prepare solids with liquid crystalline order. Vapor deposi-

tion provides access to a large variety of microstructures independent of the chemical nature of the underlying substrate; for thermal annealing to be successful, the anchoring condition imposed by the substrate must be consistent with the desired structure. In addition, thermal annealing of one layer might degrade the structure of a previously prepared layer. Vapor deposition is already a common thin film fabrication technique in industrial settings, making these findings even more pertinent. The two representative structures formed in the liquid crystalline systems investigated in this study are both potentially useful in devices⁵¹ that require different geometries. For instance, in organic field effect transistors (OFETs) where efficient charge transport is required from a source to a drain (running along the device plane) in-plane columnar structures (i.e., edge-on molecular packing motifs) are beneficial. On the other hand, for organic photovoltaic devices (OPVs) which generally have sandwich device geometries, out-of-plane columnar arrangements (face-on molecular packing) are most efficient to carry charges between the device electrodes. That these structures are accessible without consideration of the underlying substrate chemistry may be valuable in designing devices.

CONCLUSION

Glasses of three disc-shaped molecular systems were prepared by vapor deposition, including two systems that form columnar liquid crystals. For the liquid crystal systems, a range of potentially useful structural motifs were shown to be accessible by controlling the substrate temperature during deposition ($T_{\text{substrate}}$). When deposited at $T_{\text{substrate}}$ near T_g , the structures of the columnar systems were closely related to their equilibrium liquid crystal structures. Depositing at $T_{\text{substrate}} \sim 0.75 T_g$, prepared face-on packing motifs of varying levels of organization. The vapor-deposited structures could be rationalized by a mechanism in which glass packing is controlled by surface mobility; if the substrate temperature is close to T_g , molecules at the surface organize into structures preferred at the free surface of the equilibrium liquid crystal and this structure is trapped into a glassy solid.

This work provides a new method to prepare highly organized films of columnar liquid crystalline systems, extending previous work involving a smectic²⁰ liquid crystal and non-mesogens^{16,19}. This preparation technique may be useful in preparing active layers in organic electronic and optoelectronic devices. One important aspect of the work that needs further investigation is the preparation of highly organized films with controllable in-plane structure (such that all the columns are pointing along a predetermined axis in the device geometry). More work is required to move towards that goal, perhaps with the use of external fields during the deposition process to control in-plane order.

ASSOCIATED CONTENT

Supporting Information. *In-situ* scattering pattern evolution upon annealing, X-ray scattering patterns comparing crystals and glasses of the three systems, and discussion on transformation process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*ediger@chem.wisc.edu

Author Contributions

The manuscript was written through contributions of all authors.

Notes

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ABBREVIATIONS

GIWAXS, grazing incidence wide angle X-ray scattering; AFM, atomic force microscopy; UV/Vis, Ultraviolet-visible absorption spectroscopy; $T_{\text{substrate}}$, substrate temperature during deposition; T_g , the glass transition temperature.

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