

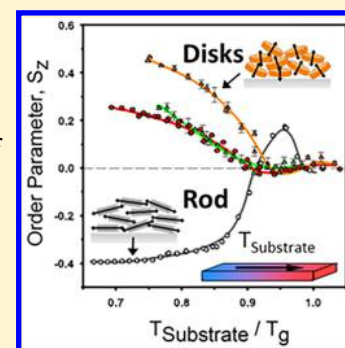
Influence of Molecular Shape on the Thermal Stability and Molecular Orientation of Vapor-Deposited Organic Semiconductors

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ABSTRACT: High thermal stability and anisotropic molecular orientation enhance the performance of vapor-deposited organic semiconductors, but controlling these properties is a challenge in amorphous materials. To understand the influence of molecular shape on these properties, vapor-deposited glasses of three disk-shaped molecules were prepared. For all three systems, enhanced thermal stability is observed for glasses prepared over a wide range of substrate temperatures and anisotropic molecular orientation is observed at lower substrate temperatures. For two of the disk-shaped molecules, atomistic simulations of thin films were also performed and anisotropic molecular orientation was observed at the equilibrium liquid surface. We find that the structure and thermal stability of these vapor-deposited glasses results from high surface mobility and partial equilibration toward the structure of the equilibrium liquid surface during the deposition process. For the three molecules studied, molecular shape is a dominant factor in determining the anisotropy of vapor-deposited glasses.



Vapor-deposited organic glasses are important materials in emerging technologies and for furthering our understanding of the amorphous state. Vapor deposition is commonly used to prepare amorphous active layers in organic electronics.^{1–3} Amorphous films are desirable because they are macroscopically homogeneous, and their properties can be tuned by changing the preparation route. In addition, vapor deposition can produce glasses with high thermal stabilities and high densities, properties that are expected to improve lifetimes for organic electronic devices.^{4–8} Furthermore, glasses produced by vapor deposition can have very low enthalpies, indicating a low position in the potential energy landscape that controls the structure and dynamics of amorphous systems.^{9,10} These materials provide unique insight into fundamental glass behavior. For instance, it appears that secondary relaxations and tunneling two-level systems are significantly suppressed in these tightly packed glasses.^{11,12}

Controlling molecular packing in crystals has been a long-standing goal for chemists, but only in the last 15 years has it been recognized that packing can also be manipulated in the amorphous state through vapor deposition. While glasses prepared by cooling a liquid inherit the isotropic structure of the liquid, early reports indicated horizontal molecular orientation in vapor-deposited glasses of several molecules.^{13,14} Yokoyama and coworkers investigated how molecular shape and other factors influence molecular orientation.^{1,15,16} They found that more anisotropic molecules produced more anisotropic glasses when deposited at room temperature. Dalal et al. systematically studied the effect of substrate temperature and found that the molecular orientation of rod-shaped molecules could be continuously controlled.¹⁷ Similar results have been reported for a two-component system with a rod-shaped molecule in an isotropic host.^{18,19} Controlling molecular orientation in vapor-deposited active

layers can improve device performance. For example, Yokoyama and coworkers reported that a glass with preferential horizontal orientation had three times higher electron mobility than an isotropic glass.²⁰ More recently, atomistic simulations of ethylbenzene have also shown how anisotropy can lead to improved charge-transport properties.²¹

Understanding the mechanism responsible for high thermal stability and anisotropic molecular orientation in vapor-deposited glasses is important for improving organic electronic devices. The remarkable stability of vapor-deposited glasses is believed to originate from enhanced mobility at the glass surface, allowing molecules near the surface to partially equilibrate before being buried by subsequent deposition;⁴ recent studies have shown that diffusion at the surface of organic glasses can be up to 8 orders of magnitude faster than in the bulk.^{22,23} More equilibrated glasses are lower in the potential energy landscape and have higher barriers for rearrangement, resulting in enhanced thermal stability.¹⁰ However, the role of surface equilibration in controlling anisotropic molecular orientation in vapor-deposited glasses is less clear. For rod-shaped organic semiconductors, it has been proposed that partial equilibration near the free surface during vapor deposition drives molecules into anisotropic configurations that are characteristic of those present at the surface of the equilibrium liquid.^{17,24} While some studies of molecules outside of the “rod-like” designation can be interpreted in this manner,^{1,25,26} there has been no systematic investigation to test the generality of this mechanism.

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Here we investigate the thermal stability and molecular orientation of vapor-deposited glasses of three disk-shaped molecules used as organic semiconductors. This is the first time that vapor-deposited glasses of disk-shaped organic semiconductors have been prepared over a wide range of substrate temperatures. We find that the vapor-deposited glasses have high thermal stability. For all three molecules, glasses prepared at a low substrate temperature are anisotropic with the unique symmetry axis having a tendency to be oriented perpendicular to the substrate. We simulate the equilibrium liquid of disk-shaped molecules and find there is a strong tendency for perpendicular orientation of the symmetry axis at the liquid surface. These findings suggest that the molecular orientation and thermal stability in these vapor-deposited glasses are both derived from partial equilibration near the surface during deposition. This mechanism is expected to apply to a wide variety of organic molecules, thereby providing a major step toward establishing overarching design principles for engineering high thermal stability and molecular orientation in vapor-deposited organic glasses.

Vapor deposition was used to prepare glasses of the three disk-shaped molecules shown in Figure 1a. Figure 1b shows three previously studied rod-shaped molecules,¹⁷ which we

utilize for comparison. All six molecules are hole-transport materials or light emitters and are of interest for organic electronic applications. A previously described high-throughput protocol was utilized to efficiently prepare glasses of the disk-shaped molecules across a wide range of substrate temperatures ($T_{\text{Substrate}}$).²⁷ Performing density functional theory (DFT) calculations, we confirmed that the three disk-shaped molecules have a central core that is very nearly planar; X-ray crystallography of a similar molecule is consistent with this result.²⁸

UV-vis absorption and spectroscopic ellipsometry were used to measure molecular orientation in the vapor-deposited glasses (see Methods). The molecules studied here have strong transition dipole moments in the plane of the disk (Figure 1a). Light polarized along the transition dipoles is more strongly absorbed than light polarized in a different direction. This leads to a change in absorbance depending on the molecular orientation of the molecules in the film, which is revealed by UV-vis absorption (Figure 1d) and spectroscopic ellipsometry.^{1,19,29,30}

Measuring samples prepared on a substrate with a temperature gradient allows for rapid characterization of glasses prepared at different substrate temperatures. The molecular orientation is quantified with an order parameter, S_z , defined in eq 1

$$S_z = \left\langle \frac{3}{2}(\hat{\mu} \cdot \hat{z})^2 - \frac{1}{2} \right\rangle \quad (1)$$

Here \hat{z} is normal to the substrate and $\hat{\mu}$ is the unique symmetry axis used to describe the molecular orientation illustrated in Figure 1c. As points of reference, a S_z value of +1 means $\hat{\mu}$ is perpendicular to the substrate, -0.5 means that $\hat{\mu}$ is parallel to the substrate, and 0 is consistent with the molecules having an isotropic distribution.

Our results indicate that vapor-deposited glasses of disk-shaped molecules have high thermal stability. Ellipsometry was used to monitor the thickness of vapor-deposited glasses during thermal ramping (Figure 2a). On heating, film thickness increases due to thermal expansion. At T_{Onset} the film rapidly increases in thickness as the vapor-deposited glass transforms to the lower density supercooled liquid. T_{Onset} is higher than T_g , indicating enhanced thermal stability. As shown in Figure 2b, vapor-deposited glasses of 2TNATA and m-MTDATA show enhanced stability when prepared over a wide range of substrate temperatures. Vapor-deposited glasses of TCTA also showed enhanced stability, but T_{Onset} values were above the range of our high-throughput heating stage and are not reported.

The molecular orientation of vapor-deposited disk-shaped molecules can be controlled using the substrate temperature during the deposition process. All three systems show similar trends when the substrate temperature ($T_{\text{Substrate}}$) is scaled by T_g , as shown in Figure 3. At substrate temperatures above $0.9T_g$, glasses of the disk-shaped molecules have an order parameter value of approximately zero, which is consistent with isotropic molecular orientation. For $T_{\text{Substrate}}$ below $0.9T_g$, the order parameter increases, indicating a tendency for the symmetry axis to be oriented perpendicular to the substrate.

The birefringence of the films, as measured by spectroscopic ellipsometry, provides an additional means to evaluate changes in the molecular orientation of vapor-deposited glasses. Birefringence is defined as the difference between the refractive index out-of-plane from the substrate, n_e , and in-plane, n_o . For

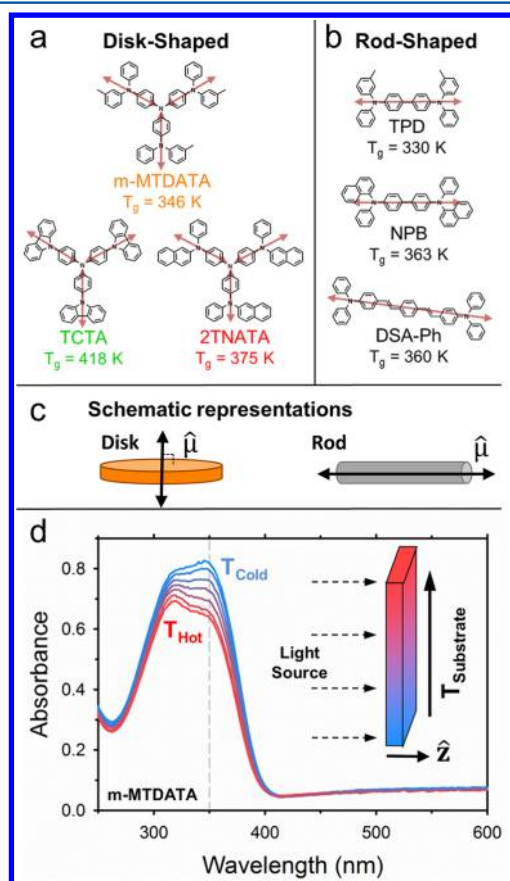


Figure 1. Molecular structures and glass transition temperatures of (a) the three disk-shaped semiconductors studied here and (b) previously studied rod-shaped compounds.¹⁷ Arrows indicate the transition dipole(s). (c) Schematic representations of disk- and rod-shaped molecules. Arrows indicate the unique symmetry axis, $\hat{\mu}$. (d) UV-vis absorbance of vapor-deposited glasses of m-MTDATA prepared at different substrate temperatures. S_z is calculated from the lowest energy absorbance, indicated with a dashed line. Inset: Schematic of the experiment.

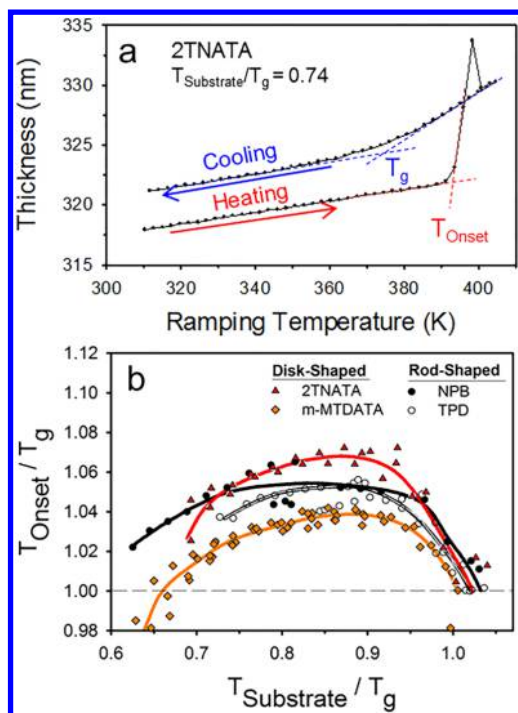


Figure 2. Thermal stability of vapor-deposited glasses of disk-shaped molecules in comparison with rod-shaped molecules. (a) Ellipsometry monitors the thickness of a vapor-deposited glass of 2TNATA during temperature ramping. The vapor-deposited glass begins to transform into the supercooled liquid above T_g at T_{Onset} indicating enhanced thermal stability. (b) Thermal stability for vapor-deposited glasses of 2TNATA and m-MTDATA prepared at different substrate temperatures. T_{Onset} and $T_{\text{Substrate}}$ are normalized by T_g to compare different molecules. Also shown are T_{Onset} values for two rod-shaped molecules reported by Dalal et al.¹⁷

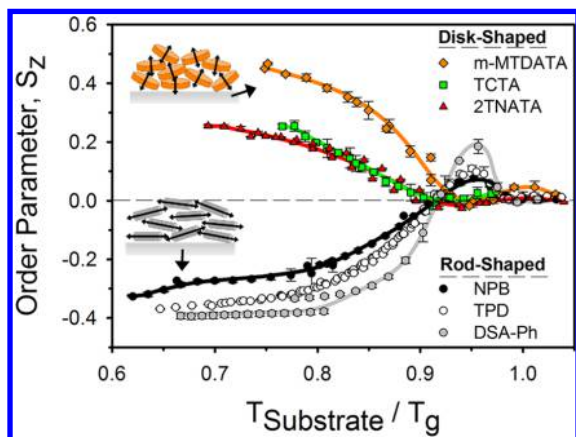


Figure 3. Order parameter, S_z , describing the average orientation of the molecular symmetry axis, $\hat{\mu}$, in vapor-deposited glasses as a function of substrate temperature during deposition. S_z is calculated from ellipsometry for 2TNATA and UV-vis for m-MTDATA and TCTA. Error bars represent 90% confidence intervals for each substrate temperature for each sample and are typically smaller than the symbol size. Rod-shaped molecules NPB, TPD, and DSA-Ph are reproduced from Dalal et al.¹⁷ Inset cartoons illustrate the molecular orientations at low $T_{\text{Substrate}}$.

vapor-deposited glasses of the three disk-shaped molecules, the birefringence can be controlled via the substrate temperature during the deposition, as shown in Figure 4. All three molecules show similar trends in birefringence when the substrate

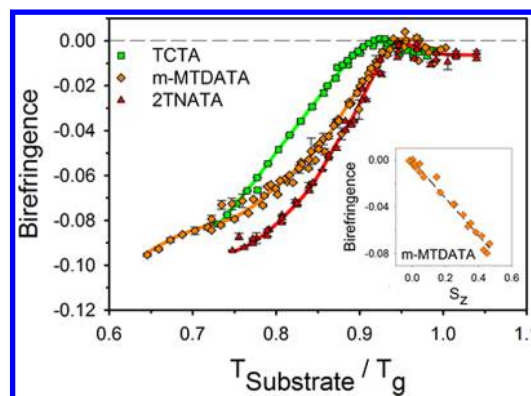


Figure 4. Birefringence of vapor-deposited glasses of three disk-shaped molecules from ellipsometric measurements. Error bars represent 90% confidence intervals for each substrate temperature and are typically smaller than the symbol size. Inset: A comparison between the birefringence and the order parameter for m-MTDATA glasses.

temperature is normalized by T_g . For these disk-shaped molecules, the birefringence and the order parameter are proportional to each other, as illustrated in the Figure 4 inset. Additionally, films with thicknesses ranging from 100 to 700 nm had birefringence values consistent with those reported in Figure 4, indicating that the molecular orientation is independent of film thickness and uniform within the film.

To enable further discussion, we briefly compare the glasses formed by disk- and rod-shaped molecules. For both disk- and rod-shaped molecules, vapor deposition produces glasses with enhanced stability over a considerable range of $T_{\text{Substrate}}/T_g$. Both disk- and rod-shaped molecules produce isotropic glasses for $T_{\text{Substrate}}/T_g$ very near unity and glasses with significant anisotropy at lower values of $T_{\text{Substrate}}/T_g$. The observation that important patterns in the data are revealed by dividing $T_{\text{Substrate}}$ by T_g immediately suggests a dominant role for molecular mobility in determining both the thermal stability and the anisotropic structure of the vapor-deposited glasses. Because bulk mobility is essentially negligible below T_g on the time scale of deposition,²² it is reasonable to focus on the much faster surface mobility as the key influence for both disk- and rod-shaped molecules. Of course, the average orientation of the molecular symmetry axes in the glasses formed by disk- and rod-shaped molecules shows quite different dependences upon $T_{\text{Substrate}}/T_g$ in Figure 3, and a detailed mechanism must explain this difference, as we discuss below. We note that the low-temperature glasses of both disk- and rod-shaped molecules show a tendency for the transition dipoles to lie in the plane of the substrate. We calculate S_z for $\hat{\mu}$ rather than for the transition dipoles to make a fundamental connection with molecular shape. Furthermore, this characterization scheme uniquely allows the orientation of disk- and rod-shaped molecules to be compared with the same limits for S_z .

The enhanced thermal stability and anisotropic molecular orientation of rod-shaped molecules have been explained in terms of partial equilibration at the free surface during deposition.^{17,24} Dalal et al. and Lyubimov et al. simulated the vapor-deposition of a coarse-grained, rod-shaped molecule at different substrate temperatures and reproduced the trends in stability and molecular orientation observed in experiments (and reproduced in Figures 2b and 3).^{17,24} High thermal stability was ascribed to increased equilibration at the glass surface. To test the extent that surface equilibration could

explain anisotropic molecule orientation, they also simulated the equilibrium liquid and found anisotropic orientation near the free surface. The simulations indicated that high surface mobility during vapor deposition allowed molecules near the free surface to partially equilibrate toward the anisotropic structure of the free surface before being buried by subsequent deposition. While others have suggested orientation mechanisms that depend on molecular shape¹ or intermolecular interactions,³¹ the mechanism discussed above is the only one that can explain how molecular orientation and thermal stability depend on $T_{\text{Substrate}}/T_g$ for rod-shaped molecules.

To test whether the above mechanism can be generalized to vapor-deposited glasses of disk-shaped molecules, we simulated the equilibrium liquid of disk-shaped molecules and calculated the molecular orientation near the free surface. Molecular dynamics simulations were performed according to procedures described in the literature,²⁴ with further details given in the Methods. For atomistic models of m-MTDATA and TCTA, Figure 5a shows the molecular orientation as a function of

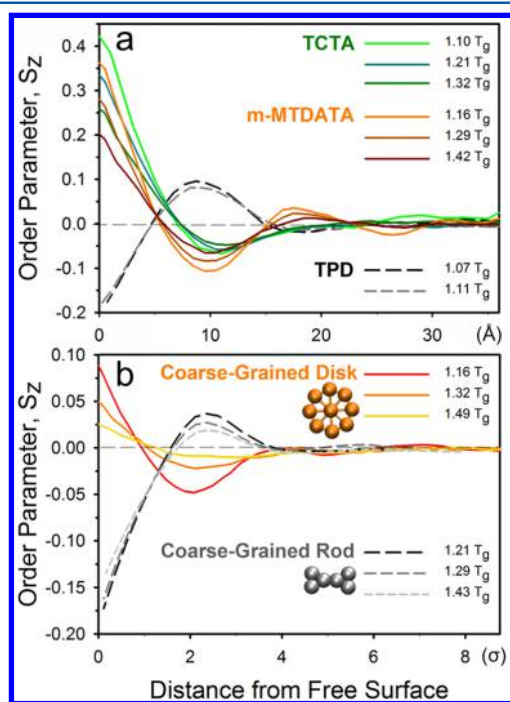


Figure 5. Molecular orientation of the molecular symmetry axis, $\hat{\mu}$, as a function of distance from the free surface of equilibrium liquids of disk-shaped and rod-shaped molecules at different temperatures. Results for rod-shaped molecules are from ref 17 and are included for comparison. (a) Atomistic simulations. (b) Simulations of coarse-grained models. Distance from the free surface is measured in terms of σ , the diameter of a Lennard-Jones bead. Inset: Structures of the coarse-grained molecules.

distance from the free surface of the equilibrium liquid at several temperatures. The free surface is defined as the depth into the film where the density is 50% that of the bulk. At the free surface the equilibrium liquids have order parameter values between 0.2 to 0.4, indicating a strong tendency for $\hat{\mu}$ to orient perpendicular to the substrate. Farther away from the free surface the order parameter decreases and shows a small valley with S_z values between -0.05 and -0.1 .

In these simulations, S_z near the surface of the equilibrium liquid significantly increases with decreasing temperature. The

simulated T_g is 388 K for m-MTDATA and 455 K for TCTA. As expected, these values are larger than the experimental T_g values due to the faster cooling rate utilized in simulations (10 K/ns vs 1 K/min).

Partial equilibration at the free surface of the glass, as described above, can explain the observed trends in thermal stability and molecular orientation for vapor-deposited glasses of disk-shaped molecules. At low substrate temperatures, surface mobility is low and only molecules very near the free surface can equilibrate. In the equilibrium liquid, molecules very near the free surface have positive order parameter values, as shown in Figure 5a. Thus, molecules near the surface adopt molecular orientations with positive order parameter values and are then trapped by subsequent deposition. This happens many times until the net result is a bulk glass with a positive order parameter value. At higher substrate temperatures, greater surface mobility allows molecules located farther away from the free surface to equilibrate during deposition. As seen in Figure 5a, there is less anisotropy away from the free surface. Molecules therefore are trapped in the glass in less anisotropic molecular orientations. During deposition at substrate temperatures above $0.9 T_g$, molecules equilibrate to depths where the equilibrium liquid exhibits a nearly isotropic molecular orientation, resulting in vapor-deposited glasses with an order parameter value of zero. The explanation given in this paragraph is consistent with the observation that molecular orientation is independent of film thickness (Figure 4). In addition, because the free surface controls the orientation eventually trapped into the glass, this mechanism predicts that the substrate chemistry is irrelevant; our experiments comparing glasses of m-MTDATA and TCTA deposited onto silicon and silica are consistent with this conclusion.

Knowledge of molecular orientation at the free surface of the equilibrium liquid allows us to understand how glasses with similarly high thermal stability (e.g., rod-like and disk-like molecules in Figure 2a) can have quite different dependences of S_z upon $T_{\text{Substrate}}/T_g$. For comparison, Figures 2, 3, and 5 show results for rod-like molecules reported by Dalal et al.¹⁷ Vapor-deposited glasses of rod-shaped molecules also show enhanced thermal stability and anisotropic molecular orientation, but they show a different temperature dependence of S_z upon $T_{\text{Substrate}}/T_g$. As shown in Figure 5a, for TPD, the equilibrium liquid exhibits negative order parameter values near the free surface. Thus at low substrate temperatures, vapor deposition leads to glasses with a negative order parameter. During deposition near $0.95 T_g$, TPD molecules are mobile down to a depth of ~ 10 Å, where the equilibrium liquid of rod-shaped molecules exhibits a small positive order parameter; consequently, vapor deposition generates glasses with a small positive order parameter. From the simulation results in Figure 5a, one might expect that deposition of disk-shaped molecules near $0.95 T_g$ would result in glasses with a small negative order parameter. The data in Figures 3 and 4 show a slight tendency in this direction, although this tendency does not exceed the uncertainty in S_z due to experimental errors.

To test the extent to which molecular shape alone controls molecular orientation in a vapor-deposited glass, we also simulated the equilibrium liquid of a coarse-grained model of a disk-like molecule. As shown in Figure 5b, the coarse-grained model consisted of a collection of nine Lennard-Jones sites connected by harmonic springs into a planar octagonal shape. Also, in Figure 5b, we see that the equilibrium liquid of the coarse-grained disk shows trends in anisotropic surface

structure similar to those observed in the atomistic simulations of m-MTDATA and TCTA: Molecules near the surface have positive order parameter values and anisotropy at the free surface increases with decreasing temperature. Previous simulations with coarse-grained rods, reproduced in Figure 5b, show similar agreement with the atomistic model of TPD.^{17,24} At a quantitative level, the simulations of coarse-grained molecules do not reproduce the magnitude of the anisotropic surface structure observed in atomistic simulations. However, the coarse-grained models do reproduce the qualitative features in the anisotropic surface structure. For the systems considered here, this suggests that molecular shape is the primary factor determining both the anisotropic surface structure of the equilibrium liquid and the anisotropic molecular orientation of the vapor-deposited glass.

These results show, for the first time, that vapor deposition of disk-shaped molecules used as organic semiconductors can prepare glasses exhibiting enhanced thermal stability and anisotropic molecular orientation over a wide range of substrate temperatures. Thermal stability and molecular orientation can be controlled by the choice of substrate temperature for the deposition process. Vapor-deposited glasses of rod-shaped molecules also demonstrate high thermal stability, but the average orientation of the molecular symmetry axis for these systems has a qualitatively different dependence on substrate temperature. For both disk-like and rod-like molecules, we attribute these observations to efficient equilibration that occurs during deposition due to high surface mobility. Partial equilibration at the glass surface during vapor deposition allows molecules to find more thermodynamically stable packing configurations (leading to high thermal stability) and also to adopt molecular orientations that are favored near the free surface. Simulations show that the symmetry axis of disk- and rod-shaped molecules orients in different ways near the free surface, and this furthers an understanding of the anisotropy of molecular orientation of the vapor-deposited glasses.

We extended the surface equilibration mechanism proposed in ref 17 for vapor-deposited glasses to disk-shaped organic semiconductors. We suggest that this mechanism will apply to a wide variety of organic molecules, regardless of molecular shape, and also to two component systems. While molecular shape is a dominant factor in determining molecular orientation in the vapor-deposited glasses of the six molecules compared here, we expect that this will not always be the case. However, even for molecules where specific interactions might overwhelm the role of molecular shape and possibly reduce surface mobility, we expect that the structure of the free surface of the equilibrium liquid will still allow a prediction of the anisotropic structure of vapor-deposited glasses. Deposition of a dilute guest molecule in a host material has been studied extensively because of the importance of emitter orientation in determining the efficiency of organic light emitting diodes. Much of the literature is in agreement with our view that the surface mobility of the host molecules is a key factor in determining emitter orientation in the glass.^{19,25,32,33} However, for organo-metallic emitters, some authors suggest that emitter orientation is slaved to host orientation,³⁴ while others suggest that the dilute emitter orientation is independent of the host material.³² In contrast, we suggest that all of these systems might be well-described by the surface equilibration mechanism; that is, we imagine that simulations of the free surface of a two-component liquid would allow an understanding of the anisotropic glasses produced by codeposition of the components. For the first

time, our work suggests a general mechanism for thermal stability and molecular orientation in vapor-deposited glasses of a wide variety of molecules, including systems commonly used in organic electronics. We expect this will guide the choice of molecule and deposition conditions for active layers in organic electronic devices.

METHODS

Samples were prepared by physical vapor deposition onto silicon and fused silica substrates using a previously described high-throughput protocol.²⁷ Molecules obtained from Sigma-Aldrich ($\geq 97\%$ purity) were evaporated in a vacuum chamber with a base pressure of 10^{-7} Torr at a rate of ~ 2 Å/s. A temperature gradient was applied to the substrate to efficiently prepare glasses over a wide range of substrate temperatures. Because of their low thermal conductivity, fused silica substrates were placed on a stainless-steel bridge, and a temperature gradient was applied to the bridge. Samples prepared at a single substrate temperature were used to calibrate the temperature of the high-throughput samples.

UV-vis absorption at normal incidence was measured in transmission at many locations across samples (70–100 nm thick) deposited onto fused silica substrates with an imposed temperature gradient. This procedure is a high-throughput version of a technique developed by Yokoyama and coworkers.³⁵ S_z was calculated from eq 2

$$S_z = 2 \left(\frac{A}{A_{\text{isotropic}}} - 1 \right) \quad (2)$$

Here A is the measured absorbance of the as-deposited glass and $A_{\text{isotropic}}$ is the absorbance of the liquid-cooled glass prepared by thermal cycling, which serves as an isotropic reference state.

Ellipsometry measurements were performed on glasses deposited onto silicon substrates using a J. A. Woollam M-2000U ellipsometer (245–1000 nm) at three angles.²⁷ For films over 100 nm, birefringence was calculated using an anisotropic Cauchy model as previously described.⁵ For films with thickness ~ 100 nm, an anisotropic oscillator model meeting previous described requirements¹⁷ was built for each material and used to determine the extinction coefficient out of the plane of the substrate (k_z) and the extinction coefficient in-plane (k_{xy}). S_z was then calculated using eq 3

$$S_z = \frac{2(k_{xy} - k_z)}{k_z + 2k_{xy}} \quad (3)$$

Equations 2 and 3 are specific to disk-shaped molecules with a symmetric in-plane arrangement of transition dipoles; we verified with DFT calculations that these assumptions are met to an excellent approximation. For 2TNATA, the oscillator model provided a satisfactory description of all the vapor-deposited glasses, and the resulting values of S_z are shown in Figure 3. A satisfactory model of the ellipsometry data was not found for m-MTDATA and TCTA, but different models agreed within $\pm 0.05 S_z$, and these results agree with the S_z values obtained by UV-vis absorption (which are presented in Figure 3).

Molecular dynamics simulations of the equilibrium liquid were performed using the GROMACS 4.6.3 simulation package as previously described.²⁴ For the atomistic systems, a free-standing film of about 800 molecules was prepared in a 8.5 nm

× 8.5 nm × 28.0 nm box, and the molecular orientation was averaged over both free surfaces. The all-atom optimized potential for liquid simulations (AA-OPLS) force field was used.^{36,37} For the coarse-grained simulations, the liquid film was on a substrate consisting of 1000 LJ beads, and the box size was $25\sigma \times 25\sigma \times 70\sigma$. The simulations were performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator package (LAMMPS) in the NVT ensemble.³⁸ Stiff harmonic potentials for angles and bonds, where $K = 1000$, were used to keep the octagonal shape with side length of 1σ for the coarse-grained disk. The same pair coefficients were used as in the coarse-grained rod simulations.^{17,24}

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Notes

The authors declare no competing financial interest.

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