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Surface Equilibration Mechanism Controls the Stability of a Model Codeposited Glass Mixture of Organic Semiconductors

Shinian Cheng, Yejung Lee, Junguang Yu, Lian Yu, and M. D. Ediger*

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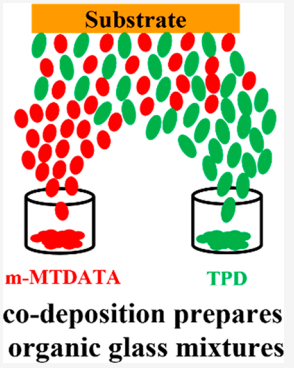
ABSTRACT: While previous work has identified the conditions for preparing ultrastable single-component organic glasses by physical vapor deposition (PVD), little is known about the stability of codeposited mixtures. Here, we prepared binary PVD glasses of organic semiconductors, TPD (*N*,*N*′-Bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine) and m-MTDATA (4,4′,4″-Tris[phenyl(m-tolyl)-amino]triphenylamine), with a 50:50 mass concentration over a wide range of substrate temperatures (T_{sub}). The enthalpy and kinetic stability are evaluated with differential scanning calorimetry and spectroscopic ellipsometry. Binary organic semiconductor glasses with exceptional thermodynamic and kinetic stability comparable to the most stable single-component organic glasses are obtained when deposited at T_{sub} = 0.78−0.90T_g (where T_g is the conventional glass transition temperature). When deposited at 0.94T_g, the enthalpy of the m-MTDATA/TPD glass equals that expected for the equilibrium liquid at that temperature. Thus, the surface equilibration mechanism previously advanced for single-component PVD glasses is also applicable for these codeposited glasses. These results provide an avenue for designing high-performance organic electronic devices.



Glasses play a central role in modern technologies, including communications,[1] pharmaceuticals,[2] and organic electronics.[3] They are amorphous solids with macroscopic homogeneity and nearly unlimited compositional flexibility. These features make glasses preferable to crystalline materials in some applications, such as organic light emitting diode (OLED) displays. The active layers in OLEDs are organic semiconductor glasses. The macroscopic homogeneity of glasses ensures smooth surfaces and uniform performance in all pixels, while the compositional flexibility of the glassy matrix facilitates the preparation of well-mixed emissive layers with tunable composition. A fundamental challenge for glass materials is their long-time stability.[4,5] Due to their non-equilibrium nature, glasses can either physically age[6] over time or undergo crystallization if chemical degradation is prevented.[7] Both may lead to degradation of the performance of the OLED device and reduce lifetime.[8] Therefore, it is practically important to produce glass materials with highly enhanced stability.

Recent studies have demonstrated that physical vapor deposition is an excellent technique to prepare glasses with exceptional thermodynamic and kinetic stability.[9−12] In addition, such ultrastable PVD glasses also exhibit high density,[13] enhanced photostability[14,15] high resistance to crystallization,[16] and high mechanical moduli.[17,18] These desirable properties cannot be obtained using other preparation techniques. It is hypothesized that surface mobility is responsible for the formation of these ultrastable glasses prepared from PVD.[11] The strongly enhanced mobility at the glass surface allows molecules to find low energy configurations before being buried by further deposition.[11] This surface equilibrium mechanism has been supported by theoretical work,[19,20] computer simulations,[21−23] and direct surface mobility measurements.[24−27] With a few exceptions,[28−30] however, the study of the stability of PVD organic glasses has been limited to single-component systems.

Some fundamental issues remain to be addressed regarding the stability of the PVD glass mixtures. It is not clear whether a mixture should form an ultrastable glass, even when the two components individually form ultrastable glasses. Based on the knowledge from single-component PVD glasses, high mobility at the surface is the key for molecules to find low energy configurations and form ultrastable glasses. However, it may be impossible to find a proper deposition temperature, at which both components for codeposition have high surface mobility simultaneously, especially when they have a large difference in T_g values. In addition, even if the two pure components can have high enough surface mobility at a given temperature, immiscibility or the capability to form hydrogen bonds between components (which would lower surface mobility) may block the formation of ultrastable mixtures. Very recent work reported that codeposited organic semiconductor glasses of 8-hydroxyquinolinolato-lithium (Liq) and 4,7-diphenyl-

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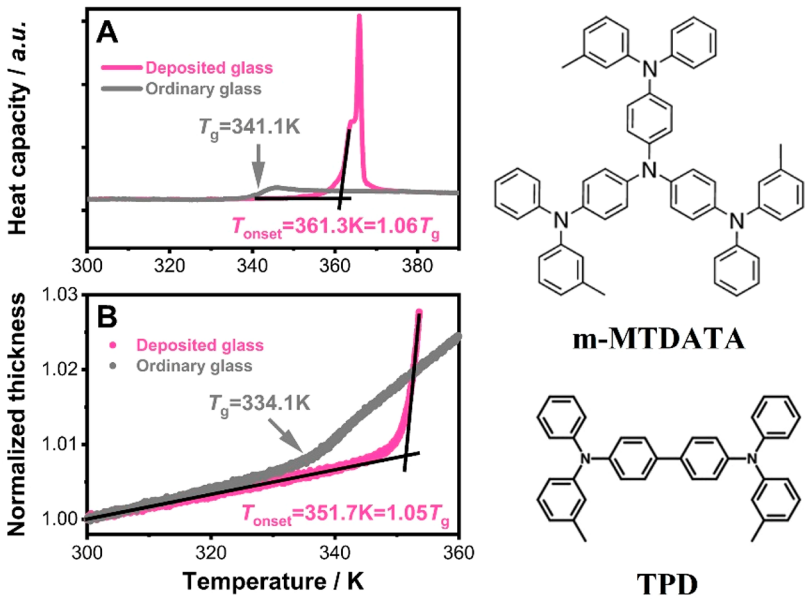

Figure 1. Temperature scanning experiments to determine the kinetic stability of codeposited m-MTDATA/TPD glasses with a mass ratio of 50:50. The binary glasses were prepared at T_{sub} = 300 K with a deposition rate 0.42 ± 0.03 nm/s. A) Heat capacity as a function of temperature determined from DSC measurements in the heating process with 10 K/min; B) Normalized film thickness as a function of temperature determined from ellipsometry ramping measurements at a heating rate of 1 K/min. The film thickness is normalized at 300 K.

1,10-phenanthroline (BPhen) do not show ultrastable properties (e.g., higher density).[30]

Understanding the properties of PVD glass mixtures is important for the technology. PVD is the standard route to prepare glassy layers of organic semiconductors in OLEDs and these layers are often mixtures. For example, the light-emitter layer is generally a glassy mixture of light-emitting molecules dispersed in a host.[31−33] Recent studies have indicated that OLEDs prepared with ultrastable vapor-deposited glass layers show extended device lifetime.[34,35] Thus, it is an important goal to understand the physical mechanisms controlling the stability of vapor-deposited glass mixtures and to identify the deposition conditions that produce highly stable multicomponent glasses.

To enrich our understanding of multicomponent PVD glasses, we codeposited binary glasses of organic semiconductors: m-MTDATA and TPD, in a wide substrate temperature (T_{sub}) range. The two components selected can form ultrastable glasses as neat materials.[36] Differential scanning calorimetry and spectroscopic ellipsometry were applied to evaluate the enthalpies and kinetic stabilities of the PVD mixtures. In this work, we focused our attention on nondilute mixtures with a mass ratio near 50:50, as we anticipate that this is the regime in which ultrastable glass formation is most challenging. We found that the stability of codeposited m-MTDATA/TPD glasses is controlled by T_{sub}/T_g (where T_g is the conventional glass transition temperature) in the same manner as single-component PVD organic glasses. When codeposited at T_{sub} = 0.78−0.90T_g, the most stable binary glasses are formed with an onset temperature being 5% higher than the conventional glass transition temperature, which is comparable to the most stable single-component organic glasses. Interestingly, the enthalpy of m-MTDATA/TPD glass deposited at 0.94T_g is equal to that expected for the equilibrium liquid at that temperature. All these results are consistent with the surface equilibration mechanism previously advanced to understand single-component PVD glasses.

The DSC results in Figure 1A demonstrate that the codeposited m-MTDATA and TPD (chemical structures shown in Figure 1) glass mixture with a 50:50 mass ratio prepared at T_{sub} = 300 K is kinetically much more stable than the corresponding liquid-cooled glass. The results for the as-deposited sample obtained in the initial heating process are presented in pink. After the as-deposited glass is completely transformed into the liquid state, the same sample is cooled by 10 K/min to form the corresponding liquid-cooled glass and then heated again, yielding the gray data. As shown in Figure 1A, the devitrification process for both deposited and liquid-cooled glass is accompanied by a significant increase in heat capacity. The onset temperature (T_{onset}) where the as-deposited glass starts to transform is 361.3K, while the glass transition temperature (T_g) characterized using the midpoint convention for the corresponding liquid-cooled glass is 341.1K. This 20.2 K difference suggests that a much higher temperature is required for the vapor-deposited sample to disrupt its glassy molecular packing, a straightforward indication of higher kinetic stability for the codeposited m-MTDATA/TPD glass. It should be emphasized that the as-deposited films are fully amorphous. The absence of crystalline material is confirmed by grazing-incidence wide-angle X-ray scattering (GIWAXS) and DSC measurements (Figures S1 and S2).

One challenge in performing calorimetric measurements on thin vapor-deposited glasses is to introduce sufficient sample mass for good thermal signals. Rodríguez-Tinoco et al.[37] addressed this issue by using aluminum foil as the substrate and then folding the foil with deposited glass into a DSC pan. In this work, we used gold foil rather than aluminum because of its better thermal conductance. We codeposited a 1200 nm organic film onto a 1.8 × 1.8 cm^2 gold foil; the foil mass was about 0.4 mg, while the sample mass was about 0.5 mg. As shown in Figure 1A, this mass is sufficient to obtain good glass transition thermal signals for our samples.

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Ellipsometry measurements reveal consistent results with the calorimetric experiments. Figure 1B shows the normalized film thickness as a function of temperature for a codeposited m-MTDATA/TPD (50:50) glass mixture at T_{sub} = 300 K. The film thickness for both as-deposited and liquid-cooled glasses increases linearly with temperature due to thermal expansion. A sharp deviation from this linear dependence was observed when the samples started to expand as they transform into a supercooled liquid. In the ellipsometry data, the obtained T_{onset} for codeposited m-MTDATA/TPD glass is 17.6K higher than the T_g for the liquid-cooled glass, consistent with high kinetic stability. It is expected that the absolute transition temperatures measured by ellipsometry are somewhat lower than those measured by calorimetry due to the lower heating rate employed.

The ratio T_{onset}/T_g is often used to quantify the kinetic stability of vapor-deposited glasses.[38] For the codeposited m-MTDATA/TPD glasses, calorimetry and ellipsometry measurements show good agreement, with T_{onset}/T_g equal to 1.06 from calorimetric experiments and 1.05 from ellipsometry measurements. Interestingly, T_{onset}/T_g = 1.05−1.06 is consistent with the values found in the most stable single-component PVD organic glasses.[38] Furthermore, the T_{sub} = 300 K used to create the ultrastable m-MTDATA/TPD glasses is equal to 0.88T_g, located in the optimal temperature region (i.e., 0.78−0.90T_g) for preparing single-component ultrastable organic glasses.[38]

The results above suggest that the surface equilibration mechanism previously advanced for single-component glasses may be applied to understand the kinetic stability of codeposited m-MTDATA/TPD glasses. To test this hypothesis, we codeposited m-MTDATA/TPD mixtures with the same mass ratio of 50:50 at five additional substrate temperatures ranging from 210 to 340 K. We present the DSC results for these codeposited glasses in Figure 2A and the results from ellipsometry measurements are shown in Figure S3. As seen from Figure 2A, the T_{onset} values for deposited glasses varies substantially with the substrate temperature used to prepare the glasses. This demonstrates that the kinetic stabilities of codeposited m-MTDATA/TPD glasses are controlled by the substrate temperatures, consistent with the surface equilibration mechanism.

Figure 2A also indicates that the enthalpy for codeposited m-MTDATA/TPD glasses with the same chemical composition is tunable. One may see that the glass transition endothermic peak area is not constant when the glass mixtures are deposited at different T_{sub}. The endothermic peak area quantifies the enthalpy required to transform the glass into an equilibrium liquid state. Figure 2B shows the enthalpy for codeposited m-MTDATA/TPD glasses as determined by integrating the heat capacity data in Figure 2A. Excluding the glass deposited at T_{sub} = 340 K, the enthalpy of codeposited glasses is significantly lower than that of the liquid-cooled glass.

The thermodynamic stability of codeposited m-MTDATA/TPD glasses can be quantitatively compared to single-component PVD glasses using the fictive temperature T_f.[11] As shown in Figure 2B, the T_f values for codeposited m-MTDATA/TPD glasses were determined from the temperature where the as-deposited glass enthalpy matches the (extrapolated) enthalpy data for the equilibrium liquid (the black curve). The m-MTDATA/TPD glass deposited at T_{sub} = 270 K has the lowest T_f = 311.1 K, which is 30 K lower than that of the ordinary liquid-cooled glass with $T_f = T_g$ = 341.1 K. This result is comparable to the most stable PVD glasses of pure TNB[11] and IMC,[39] as well amber glasses aged for tens of millions of years[40,41] whose T_f values are around 30 K lower than the glass transition temperature of the liquid-cooled glass.

Figure 3 demonstrates that the kinetic and thermodynamic stabilities of codeposited m-MTDATA/TPD glasses are correlated. As shown in this figure, codeposited m-MTDATA/TPD glasses with higher T_{onset}/T_g (i.e., higher kinetic stability) have lower T_f/T_g (i.e., lower thermodynamic energy state). The highest T_{onset}/T_g and lowest T_f/T_g values

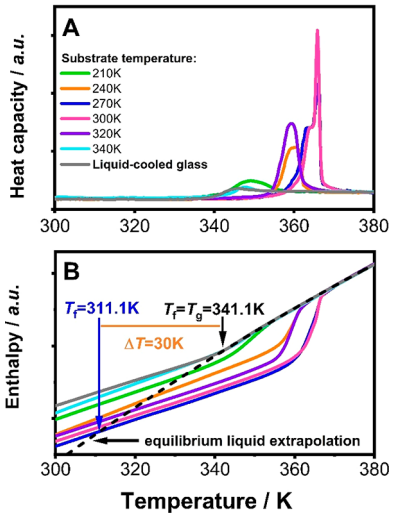

Figure 2. A) DSC heating curves for m-MTDATA/TPD mixtures codeposited at different temperatures. The gray curve denotes the result of the ordinary liquid-cooled glass; B) The enthalpy as a function of temperature for the studied m-MTDATA/TPD glasses. The heat capacity of the samples shown in panel A is integrated to obtain the enthalpy data, providing access to the fictive temperature for each sample. The dashed line is the extrapolation of the equilibrium liquid enthalpy to lower temperature by fitting the enthalpy data above T_g (from 345 to 380 K) to a quadratic function.

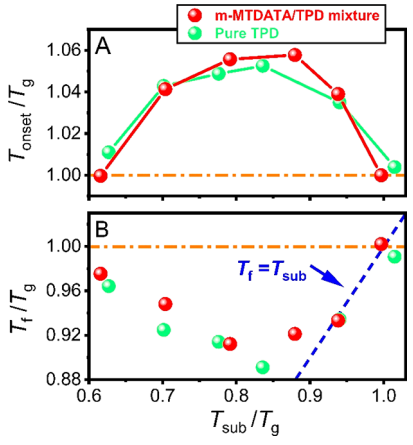

Figure 3. A) DSC results of T_{onset}/T_g for deposited m-MTDATA/TPD mixtures (red) and neat TPD (light green) glasses. The solid lines are guides to the eye; B) DSC results of T_f/T_g for deposited m-MTDATA/TPD mixtures (red) and neat TPD (light green) glasses. The blue dashed line represents the $T_{sub} = T_f$ line. The DSC heating curves for as-deposited TPD glasses and the corresponding enthalpy data are displayed in Figure S4.

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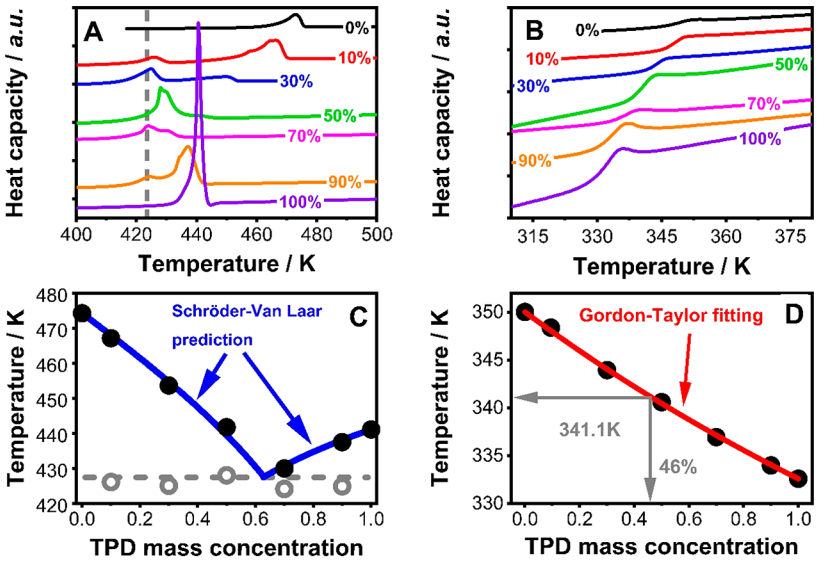

Figure 4. A) Differential scanning calorimetry thermograms of the crystalline physical mixtures of m-MTDATA/TPD with different compositions. The percentages denote the corresponding mass concentration of the TPD. B) The glass transition region is for m-MTDATA/TPD mixtures with different compositions. C) Phase diagram of m-MTDATA/TPD mixtures using experimentally determined data (circles) and a fit to the Schröder−Van Laar equation (blue curves). D) The glass transition temperature of m-MTDATA/TPD mixtures as a function of mass concentration of TPD. The black circles are experimental data determined from panel B and the red curve is a fit to the Gordon−Taylor equation.

are obtained simultaneously when m-MTDATA/TPD glasses are prepared at $T_{sub} = 0.78-0.90T_g$. These results indicate that the kinetic stability of ultrastable m-MTDATA/TPD glasses is coupled with the occurrence of low energy packing arrangements. Although this behavior has been observed in single-component organic vapor-deposited glasses,[9,38,42] it should be noted that this is not a general feature for PVD glasses. For example, the ternary metallic glass of $Zr_{65}Cu_{27.5}Al_{7.5}$ deposited at $0.8T_g$ has an enhanced kinetic stability and elastic modulus but an enthalpy higher than the corresponding liquid-cooled or annealed glasses.[17]

Moreover, the determined trends of T_{onset}/T_g and T_f/T_g as a function of T_{sub}/T_g for codeposited m-MTDATA/TPD mixtures are in good agreement with those for most organic single-component PVD glasses.[9,38,42] As an example for comparison, we added the T_{onset}/T_g and T_f/T_g values for vapor-deposited TPD glasses into Figure 3A and 3B. These values are determined on the basis of the DSC measurements. The corresponding heat capacity and enthalpy data are listed in Figure S4. As seen from Figure 3, the data points of T_{onset}/T_g (or T_f/T_g) as a function of T_{sub}/T_g for m-MTDATA/TPD mixtures (red points) exhibit the same pattern as those for pure TPD (light green points). Importantly, similar results are obtained using spectroscopic ellipsometry (Figure S5).

The nonmonotonic dependence of T_{onset}/T_g and T_f/T_g on T_{sub}/T_g revealed in Figure 3 can be understood as a result of the surface equilibration process during deposition. When the layer is deposited below T_g, there is a thermodynamic driving force to reach the equilibrium liquid state at that temperature. High surface mobility enables molecules to find low energy and high stability configurations before being buried (and immobilized) by further deposition. Direct evidence for this view is presented in Figure 3B; the fictive temperature for m-MTDATA/TPD glasses deposited at $0.94T_g$ is equal to the corresponding substrate temperature (the blue dashed line shows $T_{sub} = T_f$). At lower values of T_{sub}/T_g, there will be a larger thermodynamic driving force to form equilibrium state, but simultaneously, the surface mobility will decrease. The most stable glasses with the highest T_{onset} (or lowest T_f) are formed when high surface mobility is paired with a large thermodynamic driving force. For organic semiconductor compounds deposited at normal rates around 0.1−1 nm/s, this match typically occurs when T_{sub} is around $0.78-0.90T_g$.[36,38] At substrate temperatures lower than this, the surface mobility is not so high, and only moderately stable glasses are formed despite the presence of a larger driving force. Our conclusion that the surface equilibration mechanism explains the stability of codeposited glasses is consistent with and extends previous work that interpreted molecular orientation in codeposited glasses using this mechanism.[43,44]

It is expected that the molecular interactions between the two components will have a strong influence on the properties of the binary PVD glasses. For example, strong repulsive interaction may lead to component separation during deposition, and strong attraction may inhibit surface diffusion. For this reason, we investigated the miscibility of m-MTDATA and TPD in bulk mixtures through calorimetric measurements. Figure 4A illustrates the DSC results of the initial heating process for binary crystalline physical mixtures of m-MTDATA and TPD of different compositions. The percentages give the mass concentration of TPD in each sample. Excluding pure TPD (100% sample) and pure m-MTDATA (0% sample), two melting processes are observed in all mixtures and the lower melting point is independent of the compositions, indicating a eutectic system. Based on these measurements, we constructed the phase diagram of m-MTDATA/TPD mixtures. As seen in Figure 4C, the experimental data are in good agreement with the theoretical prediction from the Schröder−Van Laar equation, indicating that this binary system is quite close to an ideal mixture, which is miscible at any composition.

The glass transitions observed for these physical mixtures provide important checks on miscibility and composition of the PVD samples. As can be seen in Figure 4B, for each mixture, a single glass transition is observed, demonstrating the formation of a single glassy phase during cooling the molten mixture. According to these DSC data, we determined the glass

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transition temperature for m-MTDATA/TPD mixtures as a function of the TPD concentration. As shown in Figure 4D, the T_g values decrease monotonically with the increase of TPD concentration, and the Gordon−Taylor equation[45] describes the data well. Based on the Gordon−Taylor fitting curve, the codeposited m-MTDATA/TPD glasses discussed above with T_g = 341.1 K will contain 46% TPD, which is quite close to the TPD concentration of 50% determined based on deposition rate. We infer that the as-prepared PVD glasses are well-mixed, based upon the single heat capacity maximum observed in the DSC experiments (Figure 2A) and the observation that the use of the mixture T_g in Figure 3 produces good correspondence with single-component PVD glasses.

Sufficient surface mobility of both TPD and m-MTDATA molecules at temperatures of interest is the key to forming ultrastable codeposited m-MTDATA/TPD glass mixtures. Figure 5 shows the experimental surface diffusion coefficients

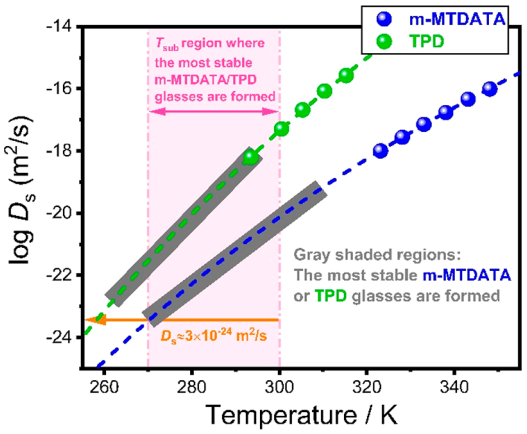

Figure 5. Surface diffusion coefficient of pure m-MTDATA (blue) and TPD (green) as a function of the absolute temperature. The D_s data for m-MTDATA and TPD were taken from ref 46 and ref 24, respectively. The dashed lines denote the Arrhenius extrapolation used to predict the D_s values at lower temperatures.

(D_s) for pure TPD[24] and m-MTDATA[46] plotted as functions of the absolute temperature. The Arrhenius equation was applied to fit the data and extrapolated to lower temperatures. The gray shaded portions of the extrapolated curves are the regions where highly stable TPD or m-MTDATA glasses are formed (using the criterion that $T_{onset}/T_g \geq 1.05$ for TPD and $T_{onset}/T_g \geq 1.04$ for m-MTDATA). Via this procedure, we estimate that the minimum D_s required to form ultrastable neat glasses of TPD and m-MTDATA is around 3×10^{-24} m^2/s. Interestingly, the D_s values for both TPD and m-MTDATA are above 3×10^{-24} m^2/s in the temperature region where the most stable codeposited m-MTDATA/TPD glasses are formed (the pink shaded region). If we assume that D_s for each component in the mixture is not too different from the pure component D_s values, our results can be rationalized by concluding that both components in the codeposited mixture must have surface mobility above some minimum value if a stable glass is to be formed. When both components have high mobility and T_{sub} is below the conventional glass transition temperature of the corresponding mixtures, we expect that low energy and high stability packing arrangements can be formed during deposition. From this perspective, a major reason why TPD and m-MTDATA can simultaneously have high mobility at the same temperatures is their comparable glass transition temperatures and ideal mixing. A mixture with strong attractive interactions (nonideal mixing) might have lower surface mobility that would interfere with stable glass formation, but the nearly ideal nature of the m-MTDATA/TPD mixture rules out this possibility. The arguments in this paragraph are based upon the assumption that surface mobility of one component is not perturbed by the presence of the second component. For stable glass formation, this is the least optimiztic scenario. If, for example, both components in a mixture were to have the same (average) surface mobility, then it would not be important that the two components had comparable T_g values. Future work that provides guidance for understanding the surface mobility of multicomponent systems would be very useful.

So far, three works have investigated the stability of vapor-deposited organic glass mixtures. In 2013, Whitaker et al. reported highly stable glasses of *cis*/*trans*-decalin mixtures across a range of compositions using *in situ* AC nanocalorimetry;[28] the two isomers in this mixture have very similar chemical structures and identical glass transition temperatures. In 2018, Qiu et al. showed that PVD produced stable glasses of 5% 4,4′-diphenylazobenzene (DPA) with 95% celecoxib.[29] The current work on m-MTDATA/TPD mixtures considerably expands upon these two papers in using organic semiconductor molecules that have different shapes and T_g values and shows that highly stable glasses are obtained even for 50/50 mixtures. In 2022, Ki et al. reported an ellipsometric study involving the stability of codeposited organic semiconductors.[30] They reported that codeposited Liq and BPhen glasses across a wide mixing ratio did not show ultrastable behavior when deposited at $0.80T_g$−$0.89T_g$. We note that Ki et al. also reported that pure Liq failed to form stable glasses via PVD. We see this as a key difference as, for the mixtures studied here, it has been confirmed experimentally that the two pure components (i.e., TPD and m-MTDATA) can form ultrastable glasses individually at proper deposition conditions.[36] The inability of a pure component to form stable glasses via PVD could be interpreted as a lack of surface mobility, which might explain why mixtures involving that component do not form stable glasses.

Given the large number of organic semiconductor mixtures used as active layers and the importance of their stability in electronic devices, it is useful to consider how general our results may be. We conclude that the surface equilibration mechanism controls the stability of codeposited m-MTDATA/TPD glasses and suggest that the following three key features are closely related to this conclusion: (i) both components can form ultrastable glasses individually via PVD; (ii) the components mix well at all compositions without strong association; (iii) the glass transition temperature difference between the components is not too large. Since many organic semiconductors can form ultrastable glasses individually when deposited under optimal conditions,[36,38,47] based on the knowledge gained here, we expect that other organic semiconductor mixtures can form ultrastable glasses when the chosen compounds have properties similar to m-MTDATA and TPD, including comparable glass transition temperatures, high miscibility, and no strong association. In addition, we anticipate that dilute mixtures of organic semiconductors, which are widely used as light-emitter layers in OLED displays, can form ultrastable glasses when deposited at around $0.85T_g$ as sufficiently dilute solutions are always miscible. This prediction is consistent with the work by Ràfols-Ribé et al.[34]

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in which OLEDs containing a codeposited dilute mixture layer prepared at $0.85T_g$ showed longer device lifetimes, if we assume that these longer lifetimes result from ultrastability.

In summary, our work presents the first case of nondilute organic semiconductor glass mixtures with exceptional thermodynamic and kinetic stability. We demonstrate that the substrate temperature controls the stability of codeposited glasses of m-MTDATA and TPD in the same way as it controls the stability of single-component PVD organic glasses. For deposition near T_g, the enthalpy is equal to that expected for the equilibrium liquid. Thus, the surface equilibration mechanism is extended to codeposited PVD glasses. We suggest that the main reasons why the PVD glasses of this binary system behave like a neat PVD glass are the ideal solution behavior and the comparable surface mobilities over the studied temperature range. In addition, both m-MTDATA and TPD are good glass formers and can individually form ultrastable glasses when deposited under proper conditions. Thus, they can be regarded as a model system to study the properties of binary PVD glasses of organic semiconductors. We expect that other organic semiconductor mixtures can form ultrastable glasses when the chosen compounds have properties similar to m-MTDATA and TPD.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00728.

Experimental materials and methods; GIWAXS patterns for codeposited m-MTDATA/TPD film (Figure S1); DSC results for codeposited m-MTDATA/TPD at T_{sub} = 270 K (Figure S2); Normalized film thickness for codeposited m-MTDATA/TPD mixtures (Figure S3); DSC results for vapor-deposited TPD (Figure S4); T_{onset} for vapor-deposited m-MTDATA/TPD mixtures and pure TPD (Figure S5) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

M. D. Ediger − *Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States;* orcid.org/0000-0003-4715-8473; Email: ediger@chem.wisc.edu

Authors

Shinian Cheng − *Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States;* orcid.org/0000-0002-5615-8646

Yejung Lee − *Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States*

Junguang Yu − *School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin 53705, United States;* orcid.org/0000-0001-6458-8307

Lian Yu − *School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin 53705, United States;* orcid.org/0000-0002-4253-5658

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.3c00728

Notes

The authors declare no competing financial interest.

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