Glass Structure Controls Crystal Polymorph Selection in Vapor-Deposited Films of 4,4 '-Bis(N-carbazolyl)-1,1 '-biphenyl

Van den Brande, Niko; Gujral, Ankit; Huang, Chengbin; Bagchi, Kushal; Hofstetter, Heike; Yu, Lian; Ediger, Mark D.

Published in:
Crystal Growth & Design

DOI:
10.1021/acs.cgd.8b00329

Publication date:
2018

Citation for published version (APA):
Van den Brande, N., Gujral, A., Huang, C., Bagchi, K., Hofstetter, H., Yu, L., & Ediger, M. D. (2018). Glass Structure Controls Crystal Polymorph Selection in Vapor-Deposited Films of 4,4 '-Bis(N-carbazolyl)-1,1 '-biphenyl. *Crystal Growth & Design*, *18*(10), 5800-5807. https://doi.org/10.1021/acs.cgd.8b00329

Glass structure controls crystal polymorph selection in vapor-deposited films of 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP)

Niko Van den Brande[a], Ankit Gujral[a], Chengbin Huang[b], Kushal Bagchi[a], Heike Hofstetter[a], Lian Yu[b], Mark D. Ediger[a]

[a] Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, USA. E-mail: ediger@chem.wisc.edu

[b] School of Pharmacy, University of Wisconsin-Madison, 777 Highland Avenue, Madison, WI 53705-2222, USA

Abstract

Glasses of a common OLED host material, 4,4′-bis(N-carbazolyl)-1,1′-biphenyl or CBP, were prepared by vapor deposition at various substrate temperatures. Consistent with previous work, the substrate temperature during deposition controls the anisotropic structure of the glass. Crystal growth at the free surface of CBP was very fast and was eliminated by covering the free surface with a thin overlayer of vapor-deposited tris-(8-hydroxyquinoline) aluminum (Alq_3). It was observed that vapor-deposited glasses of CBP with an overlayer crystallized into either the α or γ polymorph, depending on the glass structure. To our knowledge, this is the first demonstration that two glasses of the same organic compound, subjected to the same annealing conditions, grow crystals of different polymorphs. The α polymorph exhibited a fine-grained morphology, reminiscent of previous studies on glass-crystal (GC) growth, while for the γ polymorph exhibited dendritic growth. Crystals of both polymorphs grew rapidly below the glass transition temperature T_g in comparison to previously studied GC growth systems such as o-terphenyl. Surprisingly, T_g for CBP was found to be about 385 K, well above previously reported values.

1. Introduction

Amorphous solids can play two distinct roles in the world of materials. In some applications, as in the active layers in organic light emitting diodes (OLEDs), the as-prepared organic glass is the product of interest. In other situations, such as biomineralization, amorphous materials serve as an intermediate structure which conveniently holds the atoms required to build a crystal in the right place until crystallization is triggered. Whether an amorphous material fulfills the role of product or reagent, control of the crystallization process is of critical importance. For applications where glasses are preferred due to their macroscopic homogeneity, such as OLEDs, it is crucial that materials remain amorphous for the lifetime of the device. This is clearly seen by considering the emitter layer in OLED devices, composed of a host material (~90%) with dispersed emitter molecules (~10%). Many modern devices belong to the class of phosphorescent OLEDs, with emitter molecules made of heavy metal complexes[1,2]. Due to the long lifetime of the triplet state, triplet-triplet annihilation and exciton quenching by long-range diffusion to adjacent layers can occur, decreasing the quantum efficiency of such devices. In order to avoid these effects, the emitter molecules must remain dispersed in the host matrix and this is one of the crucial factors which will determine the lifetime of an OLED device[3]. Crystallization in the active layer may lead to local aggregation of emitter molecules and decreased quantum efficiency. Because of this concern, the morphological stability of OLED host materials is of significant research interest[4–6].

Physical vapor deposition allows for the preparation of amorphous layers with well-defined composition and thickness. Vapor-deposited glasses are homogeneous on a macroscopic scale, leading to smooth films that can cover a large surface. Because of these advantages, physical vapor deposition is used for the preparation of OLEDs[7]. It has been shown that controlling the temperature of the substrate (T_{sub}) during the vapor deposition process provides remarkable control of the structure and properties of the glass that is formed. High density glasses can be formed by this route and these materials have much higher activation barriers for molecular rearrangement than liquid-cooled glasses[8–12]. In addition, glasses with a considerable range of anisotropic structures can also be formed[13–16]. It is natural to ask if the better packing of vapor-deposited glasses might delay crystallization or if particular types of anisotropic packing might favor the nucleation of crystalline polymorphs with similar packing. Rodriguez-Tinoco et al. showed that surface crystal growth on vapor-deposited glasses of the pharmaceutical celecoxib was 30% slower than for liquid-cooled glasses[17]. Nakayama et al. showed that the crystallization of vapor-deposited glasses of phenyl halides depended upon the substrate temperature during deposition, with the substrate temperature modulating the time required to crystallize by as much as a factor of two[18]. To our knowledge, there are no studies that examine the influence of deposition conditions on the crystallization of glasses of organic semiconductors.

One particular organic semiconductor, 4,4′-bis(N-carbazolyl)-1,1′-biphenyl or CBP, has been used extensively as a host material in the emitter layer of OLEDs, particularly in combination with iridium complexes that are utilized as triplet state emitters[3,4]. An important disadvantage of CBP is that it is prone to crystallization when low emitter concentrations are used, resulting in a decreased device lifetime[3,4,19]. Kozlov et al. observed that the lifetime of CBP-based devices held at room temperature was limited to a few days due to crystallization. This would indicate that crystallization proceeds well below the glass transition temperature T_g for CBP. This may point towards the occurrence of glass-to-crystal or GC growth in CBP, a fast mode of crystal growth which is not limited by bulk diffusion and which is not yet completely understood[20–24]. GC growth was first described for ortho-terphenyl (OTP), and has been studied in detail for this system and a few others. The most striking feature of GC growth is that the rate of crystal growth can increase by several orders of magnitude as the temperature is lowered just a few K near T_g. Gleason et al.

determined that CBP can crystallize from solvent into three possible polymorphs (α, β, γ), where the α and γ polymorphs consist of CBP molecules with a very similar molecular conformation but different crystal packing, while the CBP molecules adopt a more twisted conformation in the β polymorph[25].

In this work, we have studied the crystallization of glasses of CBP prepared by physical vapor deposition. A range of different substrate temperatures has been utilized to prepare glasses with varying levels of anisotropy, in order to study the influence of the glass structure on crystallization behavior during subsequent isothermal annealing. In order to mimic the environment of a CBP layer in an actual OLED device, CBP glasses were covered with a thin layer of a second organic glass of tris-(8-hydroxyquinoline) aluminum or Alq_3. At 448 K, the T_g of Alq_3 significantly exceeds the crystallization temperatures studied in this work[26], and for thin vapor-deposited films of Alq_3 no crystallinity is observed for T_{sub} values below 425 K[27]. For this reason, Alq_3 can be considered as a suitably inert cover layer to enable our study of crystallization of CBP glasses.

We find that the Alq_3 overlayer effectively quenches surface crystallization of the CBP glasses and enables the study of crystal growth initiated in the bulk of the material. When different CBP glasses are annealed at 368 K, either the α or γ polymorph is formed, possibly a consequence of different glass structures. To our knowledge, this is the first demonstration that two glasses of the same organic compound, subjected to the same annealing conditions, grow crystals of different polymorphs. Both polymorphs grow at high rates, exceeding that of the well-characterized OTP at the same annealing temperature relative to T_g. Surprisingly, both calorimetry and ellipsometry measurements show that T_g for CBP is significantly higher than the values previously reported.

2. Materials & techniques

Glasses of CBP (Ossila, > 99.6% purity, used with no further purification) were prepared by physical vapor deposition at a rate of 0.2 ± 0.02 nm.s^{-1} in a high vacuum environment (base pressure on the order of 10^{-7} torr). A layer of Alq_3 (Sigma-Aldrich, > 99.995% purity, used with no further purification) was deposited on selected CBP glasses in order to quench surface crystallization. Deposition of CBP occurred on silicon substrates (with native oxide) which were maintained at selected temperatures while all Alq_3 layers were deposited at 300 K.

Ellipsometry measurements were made on a J. A. Woollam M-2000U spectroscopic ellipsometer using three angles of incidence (50°, 60°, and 70°) and a wavelength range of 500-1000 nm. Ellipsometric data were fit to models in which each deposition (CBP or Alq_3) represented a separate layer. CBP was described by an anisotropic Cauchy model while Alq_3 layers were well-described by an isotropic Cauchy model. Optical microscopy images were recorded using an Olympus BX51 microscope in reflection mode, equipped with a Lumenera INFINITY 1-1c camera and a Linkam Scientific Instruments THMS600 heating stage. Images were taken using crossed polarizers. For the isothermal annealing experiments, a 150 K.min^{-1} heating rate was used to bring the samples to the selected temperature. Wide angle X-ray scattering (WAXS) measurements were conducted on a Bruker D8 Discover diffraction instrument with an Inconel 625 alloy knife-edge installed to block air scatter. The instrument is equipped with a Cu Kα X-ray source ($\lambda = 1.54$ Å) and a VANTEC500 area detector. The incident angle was fixed at 2°, a 0.5 mm collimator was used, and the exposure time for each measurement was 1800 s. The WAXS scattering patterns presented were obtained by integrating over the azimuthal angle. WAXS patterns for CBP polymorphs were calculated from crystal structures described in literature using the freely available CCDC Mercury software[28]. Raman spectroscopy was conducted using a Thermo

Scientific DXR Raman microscope, equipped with a 780 nm laser. A PS standard was used to ensure proper calibration, and the 520.7 cm^{-1} peak of the Si substrate was used as an internal calibration check. Differential scanning calorimetry (DSC) was performed in standard aluminum pans using a TA Instruments Q2000 DSC, equipped with a refrigerating cooling system and purged with nitrogen gas.

3. Results

3.1 Glass transition temperature of CBP

In order to select a suitable substrate temperature interval for the preparation of CBP glasses by vapor deposition, DSC was performed to obtain an accurate value for the T_g. For these measurements, a DSC pan containing CBP was first heated to melt the CBP, quenched into liquid nitrogen to form a glass, and then loaded into the DSC. A scanning rate of 50 K.min^{-1} was utilized in order to clearly observe a glass transition upon heating. Although it has been reported that T_g for CBP is 335 K[29] or 351 K[30], Figure 1 shows no thermal transition near these temperatures. Instead, the glass transition was observed just before the onset of crystallization, with the midpoint of the T_g transition at approximately 385 K, and an onset at approximately 378 K. This is in agreement with the 380 K value for T_g reported for doped CBP[31], which was also consistent with interdiffusion experiments on CBP documented in a separate study[32]. A single sharp melting transition was observed at 556 K, in agreement with the reported melting point of CBP[33]. The as-supplied CBP crystals also showed a single sharp melting transition at 556 K.

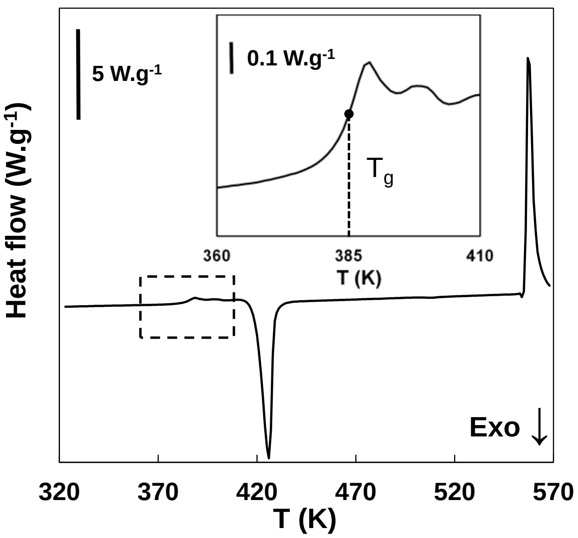


Figure 1. DSC thermogram showing the glass transition of CBP during heating at 50 K.min^{-1}. The inset enlarges the glass transition region.

In light of the disagreement between the T_g values reported in the literature and measured here by DSC, we performed ellipsometry experiments on CBP thin films. By observing the change in the thermal expansion coefficient during cooling at 1 K.min^{-1} we determined a T_g value of 379 K, in reasonable agreement with DSC, particularly given the different heating/cooling rates in the two experiments, and in good agreement with the literature value for doped CBP[31]. An example of such an ellipsometry experiment can be seen in figure S1 of the Supporting Information. Due to the propensity of CBP to crystallize quickly above T_g, it was not possible to use ellipsometry to reliably determine the densities and kinetic stabilities of the vapor-deposited glasses[15].

Because of this surprising result for T_g, additional nuclear magnetic resonance (NMR) and mass spectrometry (MS) investigations were performed which definitively confirm that the compound utilized for these experiments is pure CPB. These experiments are described in section 2 of the Supporting Information.

3.2 Structure of PVD glasses

Having established T_g for CBP, glasses were deposited over a wide T_{sub} range of 240 K to 370 K. The birefringence of these samples was measured by spectroscopic ellipsometry. As can be seen in figure 2, both positive and negative birefringence values are observed depending upon the substrate temperature during deposition. The observed pattern of birefringence vs. substrate temperature is very similar to that observed previously for vapor-deposited glasses of TPD[14,15]; given the similar shapes of these molecules, this result is expected[12,34]. By making use of this analogy, we can interpret the positive birefringence as glasses in which the long axis of CBP has a tendency towards vertical orientation while negative birefringence indicates a tendency for the long axis to lie in the plane of the substrate[15,34]. In previous studies on vapor-deposited glasses, it was shown that the birefringence is independent of film thickness in the range between 100 nm and 900 nm, indicating the molecular orientation is uniform throughout the film thickness. For the films shown in Figure 2 (and used for the rest of this work), the thickness of the CBP glasses was 900 ± 50 nm.

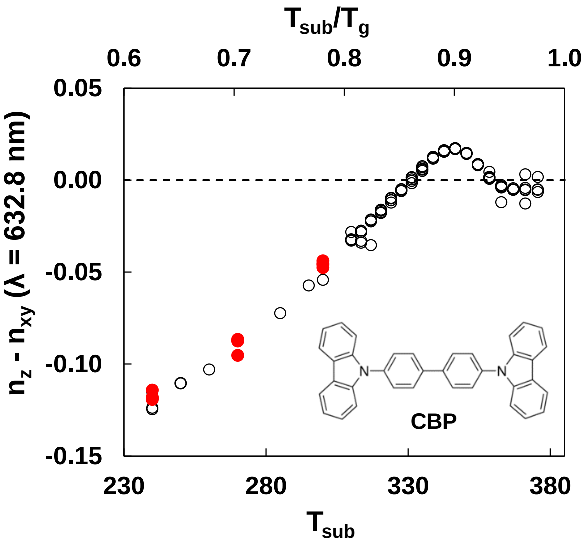


Figure 2. Birefringence of vapor-deposited glasses of CBP (structure shown as inset) as a function of substrate temperature during deposition. Here n_z is the index of refraction perpendicular to the substrate, and n_{xy} is the index of refraction in the plane of the substrate; both are measured at 632.8 nm. The birefringence of CBP glasses with free surfaces (open black symbols) and those covered by a layer of Alq_3 (solid red symbols) are very similar, as expected.

For the remainder of this study, CBP glasses prepared at three T_{sub} values (240 K, 270 K, and 300 K) will be compared. For most of our samples, an 80 ± 5 nm Alq_3 overlayer was deposited immediately after the deposition of the CBP glass. The data in figure 2 shows that this overlayer has no influence on the structure of the deposited CBP glasses, as expected. The three substrate temperatures chosen for study cover a large variation in birefringence (see figure 2), and thus glass structure. The highest T_{sub} value of 300 K (room temperature) represents the CBP glass typically used in the preparation of OLED devices. All CBP samples deposited at these substrate values were amorphous according to WAXS experiments.

3.3 Surface crystal growth

When an uncovered glass of CBP is heated, spherulites form in a matter of minutes at temperatures as low as 343 K (T_g - 42 K). This behavior is not strongly influenced by T_{sub} during deposition. When the samples are covered by an Alq_3 layer, the spherulitic growth seen without a covering layer is absent. This indicates that these spherulites were the result of surface crystallization that is eliminated by the Alq_3 overlayer. It can be expected that this type of surface crystallization is of no importance in actual OLED devices, as no free CBP surface will be present.

When CBP glasses with a free surface are annealed, in addition to surface crystallization, two additional crystal growth modes can be distinguished optically. Since these growth modes are also present in glasses capped with Alq_3, we infer that they describe crystallization in the interior of the glass and that they may be of importance for CBP layers in organic electronics devices. This study will therefore focus on the behavior of CBP glasses capped by an Alq_3 overlayer.

3.4 Polymorph selection upon annealing at 368 K

To investigate bulk crystal growth, vapor-deposited CBP glasses (with an Alq_3 overlayer) were isothermally annealed at 368 K, well below the measured T_g value for CBP. Selected optical images of the isothermal crystal growth observed at 368 K can be seen in figure 3. For glasses with T_{sub} = 300 K, crystallization at 368 K proceeds by the formation of fine-grained crystalline domains, either from the edges of the substrate or as spherulitic domains. Both the rapid rate of crystal growth below T_g and the observed morphology are reminiscent of the GC growth process (glass to crystal) described in the literature for several organic molecules[22,24,35,36]. These observations are the first indication of this phenomenon occurring in CBP. Interestingly, at this same annealing temperature, glasses prepared with T_{sub} = 240 K form morphologically different crystals. Instead of the fine-grained GC domains, dendritic crystals are formed that quickly grow into spherulites. Based on optical microscopy results, these initial spherulites are not space filling. While the rapid growth of these crystals is characteristic of previously-reported GC growth processes, their dendritic appearance is not. For glasses produced at the intermediate value of T_{sub} = 270 K (not shown), the observed morphology is less straightforward. In some cases, both types of crystals appear to grow in different parts of the sample, while for other samples only the fine-grained crystals are observed.

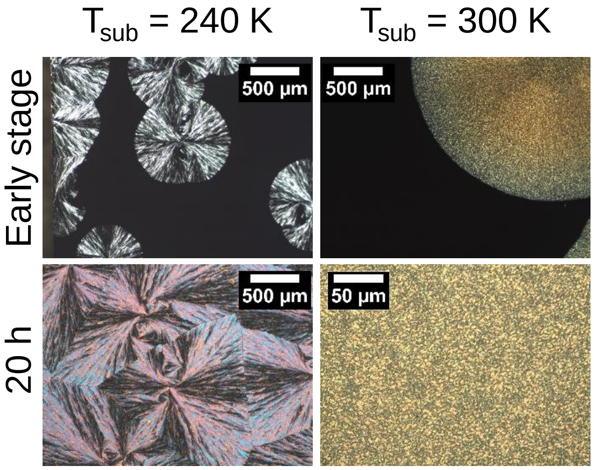


Figure 3. Polarized optical microscopy images of CBP glasses vapor-deposited at T_{sub} = 240 K (left) and T_{sub} = 300 K sample (right), when isothermally annealed at 368 K. For T_{sub} = 240 K, dendritic crystals are observed throughout the sample within the first 5 min (top), but these crystals appear to thicken afterwards, as can be seen after 20 h (bottom). For T_{sub} = 300 K, a fine-grained morphology characteristic of GC growth is seen, here shown after 60 min (top). The fine-grained morphology is largely unchanged with time as illustrated in a (further-magnified) image obtained after 20 h (bottom).

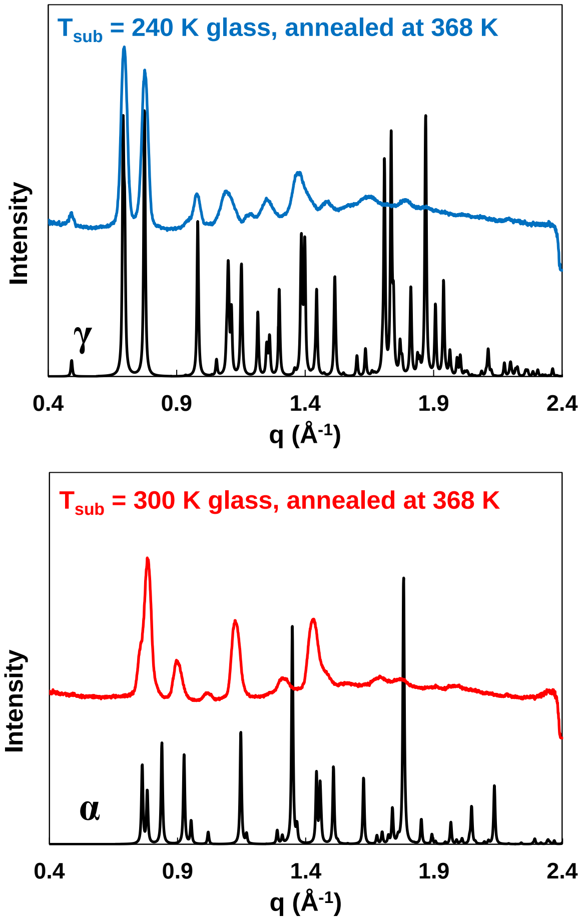


Figure 4. WAXS patterns for CBP crystals obtained from glasses prepared with T_{sub} = 240 K (top) and T_{sub} = 300 K sample (bottom), after 20 h of isothermal annealing at 368 K. Calculated scattering patterns for the α and γ polymorphs of CBP are included for comparison[25].

To further investigate the crystals obtained from glasses prepared at T_{sub} = 240 K and 300 K, samples annealed at 368 K for 20 hours were studied using WAXS and Raman spectroscopy. As can be seen in figure 4, these samples show different WAXS scattering patterns, indicating different crystal structures. A comparison of the two scattering patterns on a common axis, as well as a comparison of the two scattering patterns with their respective glasses can be found in Figures S5 and S6 of the Supporting Information. It can be see that even after 20 h of isothermal annealing, some amorphous background is still present in the T_{sub} = 240 K sample. This may be linked to the observations made by optical microscopy, where these crystals did not seem to be space filling during the early stages of crystallization. Comparing to literature scattering patterns[25], the dendritic crystals that grow from the $T_{sub} = 240$ K glass can clearly be identified as the γ polymorph. Some of the residual differences between the observed and the predicted patterns are attributed the different temperatures at which our WAXS pattern was measured (295 K) and the single-crystal structure was solved (90 K). The fine-grained crystals formed in the $T_{sub} = 300$ K sample on the other hand, show a scattering pattern which shows similarities to that expected for the α polymorph. Again, some of the differences arise from the temperature effect on lattice spacings. Based on the obtained scattering pattern, it can however not be decided whether the formed crystals correspond to the α polymorph, or to a new polymorph which has not yet been reported in literature. For the remaining discussion the term α polymorph will be used to refer to the fine-grained crystals formed in the $T_{sub} = 300$ K sample annealed at 368 K. The scattering pattern obtained on the $T_{sub} = 300$ K glass after annealing is very similar to that observed for the as-received CBP material (see figure S7 in Supporting Information).

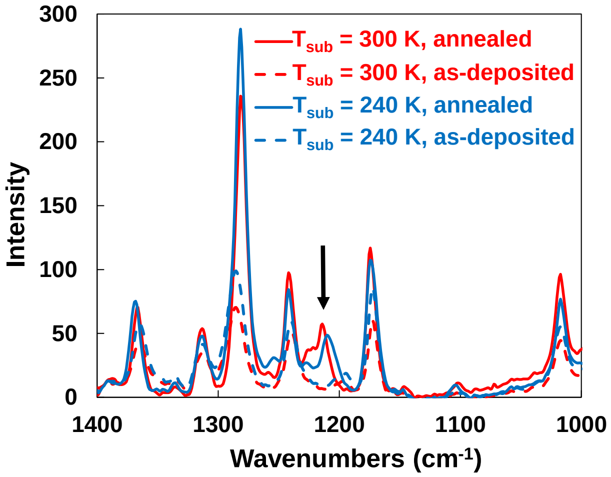


Figure 5. Raman spectra of CBP samples prepared by vapor deposition at T_{sub} = 240 K and T_{sub} = 300 K, as-deposited and after 20 h annealing at 368 K. Upon crystallization, peaks emerge near 1210 cm^{-1} that clearly differ depending upon substrate temperature during deposition.

From Raman spectroscopy, the polymorphs that result from annealing CBP glasses at 368 K can be distinguished from each other by the shapes of the peaks near 1210 cm^{-1} and by some small peak shifts (see figure 5). The similar molecular conformation of the CBP molecules in the α and γ polymorphs[25] is expected to only lead to small differences in the 500 - 1500 cm^{-1} range investigated. (More significant differences may be present at low wavenumbers due to lattice phonons, which are sensitive to crystal packing, but their study would require different Raman spectroscopy equipment[37,38].) Nevertheless, the difference in Raman spectra between the two samples offers further evidence that two different polymorphs are formed. Similar to the WAXS results, the Raman spectrum attributed to the α polymorph closely resembles that of the as-received CBP material (see figure S10 in Supporting Information). No Raman spectra for CBP polymorphs are available in literature for comparison.

Based upon the optical microscopy, WAXS, and Raman results, we conclude that different polymorphs are formed when two different glasses of CBP (vapor-deposited at two different substrate temperatures) are subjected to identical annealing. Deposition at 240 K yields a glass that clearly forms the γ polymorph upon annealing at 368 K. On the other hand, annealing of the glass deposited at 300 K most likely yields the α polymorph. In any case, crystals prepared by this later route are very similar to the as-supplied CBP material, which is a single polymorph based upon the single melting point observed upon heating. Further evidence that the glasses deposited at 240 K and 300 K yield different polymorphs upon annealing is supplied by experiments in which crystals prepared by these routes were heated under the polarizing microscope. The crystals identified above as the γ polymorph transformed into different crystals, starting around 473 K. At 556 K, these newly formed crystals melted; this is the melting point of the as-supplied CBP material. On the other hand, when the film that we have identified as containing the α polymorph is heated, it only exhibits an increase in grain size before melting at 556 K. As a final test, we subjected the film containing the γ polymorph to annealing for one hour at 473 K. Upon cooling to room temperature, WAXS indicates a scattering pattern consistent with the one that we have identified as the α polymorph.

We attempted to characterize the polymorphs formed at the earliest stages of crystallization shown in Figure 3. Using Raman spectroscopy, the crystallized domains in the samples deposited at 300 K can be clearly identified as the same polymorph which is present in these samples after 20 hours of annealing. In contrast, when samples deposited at 240 K were annealed for short times, there was no appreciable change in the Raman spectrum. This is another indication that crystals of the γ polymorph are initially not space filling.

An interesting question is whether the difference in glass structure, as indicated by the difference in birefringence (see subsection 3.2), can be linked the anisotropy of the packing in the crystal unit cells. For this purpose, the 2D WAXS diffractograms as well as integrations centered around q_z and q_z ± 35° (see figures S8 and S9 in the Supporting Information) were investigated. As the broad scattering peaks hampered the indexing of crystal planes, it was however not possible to establish a definitive connection. Nevertheless this hypothesis may hold true, and investigating the link between glass anisotropy and the anisotropy of crystal unit cell packing is an interesting future research topic.

3.5 Polymorph selection upon isothermal annealing between 358 K and 378 K

Up to this point, we have only described experiments in which the Alq_3 covered CBP glasses were isothermally annealed at 368 K. We now consider the results of isothermal annealing experiments at four other temperatures between 358 K and 378 K. These results are summarized in table 1. For glasses prepared at three different substrate temperatures, we show which crystal polymorphs form in the early stages of isothermal annealing. Except for those samples annealed at 368 K (details given above), polymorphs were identified primarily on the basis of the morphology observed in the optical microscope.

Table 1 indicates that the annealing temperature has a non-trivial impact on polymorph selection. For each of the three different glasses, annealing at low temperature yields the α polymorph while annealing at high temperature yields the γ polymorph. However, the temperature at which the transition is made from one polymorph to the other depends systematically on the substrate temperature used to prepare the glass. Under conditions where both polymorphs are indicated in the table, the results from replicate experiments were not completely reproducible, i.e., sometimes both polymorphs were observed while other times only a single polymorph was observed. It seems that polymorph selection in this transition regime is very sensitive to the structure of the glass. Regardless, these results indicate that the structure of pure CBP glasses can be controlled in such a way that either the α or the γ polymorph is formed during subsequent isothermal annealing.

Table 1: CBP polymorphs formed as a function of substrate temperature during deposition and isothermal annealing temperature. For combinations where both polymorphs are listed, no single polymorph was reproducibly observed for multiple vapor-deposited samples.

T_{iso} (K) / T_{sub}(K)	358	362	368	373	378
240	α	α+γ	γ	γ	γ
270	α	α	α+γ	γ	γ
300	α	α	α	α+γ	γ

Additional experiments indicate that polymorph nucleation likely occurs in the interior of the vapor-deposited CBP glasses and not at an interface. While we could not directly test this with optical microscopy due to limited resolution, we indirectly reach this conclusion by comparing experiments in which the interfaces had been modified. We prepared CBP glasses that were capped with sputtered gold rather than Alq_3. In other experiments, we prepared CBP glasses that were sandwiched in between Alq_3 layers. In all of these experiments, surface crystallization was effectively suppressed and polymorph selection was not influenced. Since these experiments change the nature of both the top and bottom interfaces of the CBP glasses without influencing polymorph selection, we conclude that nucleation is unlikely to occur at one of these interfaces.

We searched for conditions in which CBP crystallization could be significantly delayed by preparing a glass with a particular structure. We observed that crystallization of the T_{sub} = 240 K glasses into the α polymorph always occurred on the edges of the Si substrate. For the other two value of T_{sub} investigated, crystals formed randomly in the film as well as at the edges. This may indicate that nucleation of the α polymorph is being hindered for glasses deposited at low T_{sub}. These results suggest that in perfectly deposited films, where edge effects or obvious defects are absent, crystallization of the α polymorph may proceed significantly slower. This might effectively stabilize the CBP glass as long as the temperatures is below 368 K. Of course, in OLED devices an emitter molecule is typically co-deposited with CBP and the effect of the emitter on nucleation must also be considered.

3.6 Crystal growth rates

During the isothermal crystallization experiments discussed in the previous section, a preliminary study of crystal growth rates was conducted for the α and γ polymorphs at three temperatures, as summarized in figure 6. Growth rates were determined by measuring the size increase of γ dendrites or α fine-grained domains, where growth rates at the edges of the substrate or in spherulitical domains were essentially the same. Even from this preliminary study it is clear that both polymorphs show high growth rates. The γ polymorph crystallizes noticeably faster than the α polymorph, exceeding 10^{-6} $m.s^{-1}$ at all tested temperatures. As shown in the figure, this is significantly faster than the rates documented for o-terphenyl (OTP)[21], the best-characterized system exhibiting GC growth. Systems exhibiting faster GC growth are known, such as testosterone propionate [35,39], for which the largest GC growth rates up to this time have been reported, which are similar to those observed for CBP in this work. It should be noted however that the growth rates for CBP were obtained at lower temperatures relative to $T_{g,,}$ than the comparable GC growth rates of testosterone propionate. This warrants further study of CBP, as it may help to elucidate the mechanism responsible for bulk crystallization below T_g. We emphasize that the growth rates reported in Figure 6 were obtained for CBP films capped with Alq_3 and thus represent bulk crystal growth rates. Surface crystal growth rates observed for uncapped films were even higher but are not reported here.

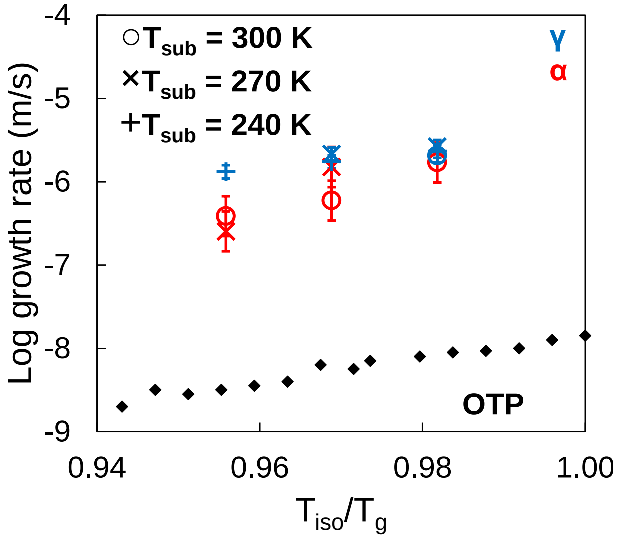


Figure 6. Isothermal crystal growth rates for CBP glasses prepared at different T_{sub}, as a function of the isothermal annealing temperature. Growth rate for both the α and γ polymorphs are shown. Error bars are ± 1 σ. For comparison, GC growth rates for o-terphenyl (OTP)[21] are shown, with the temperature scale normalized to T_g.

4. Discussion

The results presented in Figures 3-5 and Table 1 are consistent with the view that the structures of the three vapor-deposited CBP glasses determine whether the α or γ polymorph is formed during subsequent isothermal annealing. To our knowledge, this is the first demonstration that control of the structure of an organic glass can be used to produce different crystal polymorphs. Figure 2 shows that the three vapor-deposited CBP glasses investigated here exhibit quite different levels of anisotropic packing. We speculate that the anisotropic packing of molecules in the glass controls the relative rates at which the two polymorphs nucleate.

Two very recent papers have presented results which are closely connected to the work presented here. Fielitz and Holmes showed that glasses of rubrene prepared by vapor deposition can crystallize into different polymorphs depending on subsequent temperature treatment[40]. Each of our three glasses also shows this behavior. We have shown in addition that glasses with different structures can yield different polymorphs even when subjected to the same thermal treatment. Stone et al. recently reported the influence of glass structure on polymorph selection for an inorganic oxide[41]. Pulsed laser deposition was used to prepare glasses of VO_2, and the pulse rate was varied to yield glasses with different structures. Upon annealing, the material deposited at a lower rate formed a metastable crystal structure in addition to the stable phase that was expected, while the material deposited at a higher rate only formed the stable crystal phase[41]. The authors attributed this behavior to a difference in the structure of the amorphous VO_2 films prepared at different rates. According to our understanding of physical vapor deposition, lowering the deposition rate can be expected to have a similar effect on glass structure as increasing the substrate temperature[15]. Thus our work is similar to that of reference 36, except that we observed complete polymorph selectivity at early times and also different types of materials were studied.

We wish to distinguish the results presented here from previous work that established that the substrate can determine polymorph selection for organic materials. For example, different polymorphs of pentacene can be observed depending upon the identity of the underlying substrate[42]. Such substrate-induced phases are not necessarily the effect of epitaxy, but are more broadly the result of interaction between the structure and the anisotropic molecule. This type of interaction cannot explain our results. We observe that different glasses on the same surface yield different polymorphs. Furthermore, as consistent polymorph selection was obtained with different underlayers (Alq_3 and native oxide on silicon) and overlayers (Alq_3 and gold), it is reasonable to conclude that polymorph selection happens in the bulk of the glass and not at one of the interfaces.

In our experiments, we expect that nucleation occurs during isothermal annealing and not during the deposition of the CBP glasses. Each of the three glasses forms different polymorphs at different annealing temperatures, which would not be expected if nucleation of a specific polymorph occurred during deposition. The observation that crystal growth rates are similar for both polymorphs rules out explanations in which nuclei of both polymorphs co-exist but yield only one observable polymorph.

Recent work on biomineralization has a conceptual connection with the idea that crystal structure can be manipulated through glass structure. The impact of an amorphous precursor phase on crystal nucleation has been widely studied in solution, and is often explained through a two- or multi-step nucleation mechanism[43,44]. This mechanism is of specific importance for biomineralization, where a transient amorphous phase may be responsible for inducing different crystal orientations and even polymorphs[45]. For example, it has been reported that short-range order in X-ray amorphous precursors of biominerals may determine the polymorph of the final crystalline product[45].

There is an alternative interpretation of the results presented here that emphasizes the role of compressive stress. A compressive stress in a vapor-deposited glasses may be induced when the temperature is increased for annealing. This occurs because the thermal expansion coefficient of the silicon substrate is very small; when the temperature is increased, the attached organic glasses are inhibited from their normal lateral expansion by the substrate. If we imagine that vapor deposition produces a glass that is free of stress at the deposition temperature, then the glass deposited at the lowest temperature will have the greatest compressive stress at a given annealing temperature. It has been proposed that stress can influence both the rate of nucleation[46] and the crystal growth rate[47]. Future experiments on substrates with larger thermal expansion coefficients could test this hypothesis. While the compressive stress in the three CBP glasses investigated here is unknown, we do know that these glasses have quite different structures (Figure 2). For this reason, we currently favor the explanation that glass structure controls polymorph nucleation.

5. Conclusion

CBP glasses with varying levels of structural anisotropy can be formed by controlling the substrate temperature during physical vapor deposition. This behavior is very similar to that observed previously for other organic glass formers, including the structurally similar TPD. By quenching the surface crystal growth of vapor-deposited glasses of CBP (using deposition of a thin glassy overlayer of Alq_3), the bulk crystallization process below T_g could be studied. This type of crystal growth is considered to be of interest for actual OLED devices, where the active layer based on the CBP host material is covered by several other organic layers. It was found that two polymorphs of CBP, α and γ, could be formed depending on the isothermal annealing temperature. Interestingly, the substrate temperature during deposition has an influence on which polymorph forms. During isothermal annealing at 368 K, the CBP glass deposited at T_{sub} = 240 K formed the γ polymorph while the glass deposited at T_{sub} = 300 K formed the α polymorph. This is a clear indication that the structure of the glass created through vapor deposition can influence the crystallization process. To the best of our knowledge, this is the first time two glasses of the same organic compound have nucleated different polymorphs when subjected to the same annealing conditions. Furthermore, the α polymorph was seen to form fine-grained crystals similar to the GC growth mode described for several organic systems. This likely indicates that CBP can crystallize via GC growth; this would be the first example of a molecule of interest to the field of OLEDs that shows this behavior. The γ polymorph on the other hand was always seen to crystallize into dendritic crystals that are not space-filling at early stages of crystallization. Preliminary measurements of the crystal growth rates for both polymorphs yield growth rates amongst the highest observed for GC growth. Finally, ellipsometry and calorimetry measurements agree that the T_g of CBP is near 385 K, significantly above the previously reported values.

Supporting Information

Ellipsometric determination of CBP T_g, NMR, MS, additional WAXS scattering patterns, WAXS 2D detector images, additional Raman spectra

Acknowledgements

NVdB was supported by a Fellowship of the Belgian American Educational Foundation. MDE and KB were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, Award DE-SC0002161. LY, CH, and AG were supported by the US National Science Foundation through the University of Wisconsin Materials Research Science and Engineering Center (DMR-1720415). Instrumentation in the Paul Bender Chemical Instrumentation Center was supported by NIH 1S10 OD020022-1 (Thermo Q Exactive™ Plus) and by a generous gift from Paul J. and Margaret M. Bender (Bruker Avance III 500).

References

(1) Hu, J.; Zhang, G.; Shih, H.-H.; Jiang, X.; Sun, P.; Cheng, C.-H. Synthesis of a Highly Phosphorescent Emitting iridium(III) Complex and Its Application in OLEDs. *J. Organomet. Chem.* **2008**, *693*, 2798–2802.

(2) Tan, G.; Chen, S.; Sun, N.; Li, Y.; Fortin, D.; Wong, W.-Y.; Kwok, H.-S.; Ma, D.; Wu, H.; Wang, L.; Harvey, P. D. Highly Efficient Iridium(iii) Phosphors with Phenoxy-Substituted Ligands and Their High-Performance OLEDs. *J. Mater. Chem. C* **2013**, *1*, 808.

(3) Tao, Y.; Yang, C.; Qin, J. Organic Host Materials for Phosphorescent Organic Light-Emitting Diodes. *Chem. Soc. Rev.* **2011**, *40*, 2943.

(4) Smith, A. R. G.; Ruggles, J. L.; Cavaye, H.; Shaw, P. E.; Darwish, T. A.; James, M.; Gentle, I. R.; Burn, P. L. Investigating Morphology and Stability of Fac-Tris (2-phenylpyridyl)iridium(III) Films for OLEDs. *Adv. Funct. Mater.* **2011**, *21*, 2225–2231.

(5) Zhang, Y.; Aziz, H. Influence of the Guest on Aggregation of the Host by Exciton–Polaron Interactions and Its Effects on the Stability of Phosphorescent Organic Light-Emitting Devices. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14088–14095.

(6) Yu, H.; Zhang, Y.; Cho, Y. J.; Aziz, H. Exciton-Induced Degradation of Carbazole-Based Host Materials and Its Role in the Electroluminescence Spectral Changes in Phosphorescent Organic Light Emitting Devices with Electrical Aging. *ACS Appl. Mater. Interfaces* **2017**, *9*, 14145–14152.

(7) Jou, J.; Kumar, S.; Agrawal, A.; Li, T.; Sahoo, S. Approaches for Fabricating High Efficiency Organic Light Emitting Diodes. *J. Mater. Chem. C* **2015**, *3*, 2974–3002.

(8) Swallen, S. F.; Kearns, K. L.; Mapes, M. K.; Kim, Y. S.; McMahon, R. J.; Ediger, M. D.; Wu, T.; Yu, L.; Satija, S. Organic Glasses with Exceptional Thermodynamic and Kinetic Stability. *Science* **2007**, *315*, 353–356.

(9) Dawson, K.; Kopff, L. A.; Zhu, L.; McMahon, R. J.; Yu, L.; Richert, R.; Ediger, M. D. Molecular Packing in Highly Stable Glasses of Vapor-Deposited Tris-Naphthylbenzene Isomers. *J. Chem. Phys.* **2012**, *136*, 94505.

(10) Dalal, S. S.; Sepúlveda, A.; Pribil, G. K.; Fakhraai, Z.; Ediger, M. D. Density and Birefringence of a Highly Stable Α,α,β-Trisnaphthylbenzene Glass. *J. Chem. Phys.* **2012**, *136*, 204501.

(11) Dalal, S. S.; Fakhraai, Z.; Ediger, M. D. High-Throughput Ellipsometric Characterization of Vapor-Deposited Indomethacin Glasses. *J. Phys. Chem. B* **2013**, *117*, 15415–15425.

(12) Ediger, M. D. Perspective: Highly Stable Vapor-Deposited Glasses. *J. Chem. Phys.* **2017**, *147*, 210901.

(13) Yokoyama, D.; Setoguchi, Y.; Sakaguchi, A.; Suzuki, M.; Adachi, C. Orientation Control of Linear-Shaped Molecules in Vacuum-Deposited Organic Amorphous Films and Its Effect on Carrier Mobilities. *Adv. Funct. Mater.* **2010**, *20*, 386–391.

(14) Gujral, A.; O'Hara, K. A.; Toney, M. F.; Chabinyc, M. L.; Ediger, M. D. Structural Characterization of Vapor-Deposited Glasses of an Organic Hole Transport Material with X-Ray Scattering. *Chem. Mater.* **2015**, *27*, 3341–3348.

(15) Dalal, S. S.; Walters, D. M.; Lyubimov, I.; de Pablo, J. J.; Ediger, M. D. Tunable Molecular Orientation and Elevated Thermal Stability of Vapor-Deposited Organic Semiconductors. *Proc. Natl. Acad. Sci.* **2015**, *112*, 4227–4232.

(16) Gómez, J.; Jiang, J.; Gujral, A.; Huang, C.; Yu, L.; Ediger, M. D. Vapor Deposition of a Smectic Liquid Crystal: Highly Anisotropic, Homogeneous Glasses with Tunable Molecular Orientation. *Soft Matter* **2016**, *12*, 2942–2947.

(17) Rodríguez-Tinoco, C.; Gonzalez-Silveira, M.; Ràfols-Ribé, J.; Garcia, G.; Rodríguez-Viejo, J. Highly Stable Glasses of Celecoxib: Influence on Thermo-Kinetic Properties, Microstructure and Response towards Crystal Growth. *J. Non. Cryst. Solids* **2015**, *407*, 256–261.

(18) Nakayama, H.; Ohta, S.; Onozuka, I.; Nakahara, Y.; Ishii, K. Direct Crystallization of Amorphous Molecular Systems Prepared by Vacuum Deposition: X-Ray Studies of Phenyl Halides. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1117–1124.

(19) Kozlov, V. G.; Bulovic, V.; Burrows, P. E.; Baldo, M.; Khalfin, V. B.; Parthasarathy, G.; Forrest, S. R.; You, Y.; Thompson, M. E. Study of Lasing Action Based on Förster Energy Transfer in Optically Pumped Organic Semiconductor Thin Films. *J. Appl. Phys.* **1998**, *84*, 4096–4108.

(20) Greet, R. J.; Turnbull, D. Glass Transition in O -Terphenyl. *J. Chem. Phys.* **1967**, *46*, 1243–1251.

(21) Hikima, T.; Adachi, Y.; Hanaya, M.; Oguni, M. Determination of Potentially Homogeneous-Nucleation-Based Crystallization in O -Terphenyl and an Interpretation of the Nucleation-Enhancement Mechanism. *Phys. Rev. B* **1995**, *52*, 3900–3908.

(22) Sun, Y.; Xi, H.; Chen, S.; Ediger, M. D.; Yu, L. Crystallization near Glass Transition: Transition from Diffusion-Controlled to Diffusionless Crystal Growth Studied with Seven Polymorphs. *J. Phys. Chem. B* **2008**, *112*, 5594–5601.

(23) Yu, L. Polymorphism in Molecular Solids: An Extraordinary System of Red, Orange, and Yellow Crystals. *Acc. Chem. Res.* **2010**, *43*, 1257–1266.

(24) Powell, C. T.; Xi, H.; Sun, Y.; Gunn, E.; Chen, Y.; Ediger, M. D.; Yu, L. Fast Crystal Growth in O-Terphenyl Glasses: A Possible Role for Fracture and Surface Mobility. *J. Phys. Chem. B* **2015**, *119*, 10124–10130.

(25) Gleason, C. J.; Cox, J. M.; Walton, I. M.; Benedict, J. B. Polymorphism and the Influence of Crystal Structure on the Luminescence of the Opto-Electronic Material 4,4′-bis(9-Carbazolyl)biphenyl. *CrystEngComm* **2014**, *16*, 7621–7625.

(26) Naito, K.; Miura, A. Molecular Design for Nonpolymeric Organic Dye Glasses with Thermal Stability: Relations between Thermodynamic Parameters and Amorphous Properties. *J. Phys. Chem.* **1993**, *97*, 6240–6248.

(27) Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Masciocchi, N.; Sironi, A. Correlation between Molecular Packing and Optical Properties in Different Crystalline Polymorphs and Amorphous Thin Films of Mer -Tris(8-hydroxyquinoline)aluminum(III). *J. Am. Chem. Soc.* **2000**, *122*, 5147–5157.

(28) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. Mercury CSD 2.0 – New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.

(29) Tsai, M.-H.; Hong, Y.-H.; Chang, C.-H.; Su, H.-C.; Wu, C.-C.; Matoliukstyte, A.; Simokaitiene, J.; Grigalevicius, S.; Grazulevicius, J. V.; Hsu, C.-P. 3-(9-Carbazolyl)carbazoles and 3,6-Di(9-Carbazolyl)carbazoles as Effective Host Materials for Efficient Blue Organic Electrophosphorescence. *Adv. Mater.* **2007**, *19*, 862–866.

(30) Ho, M.-H.; Balaganesan, B.; Chu, T.-Y.; Chen, T.-M.; Chen, C. H. A Morphologically Stable Host Material for Efficient Phosphorescent Green and Red Organic Light Emitting Devices. *Thin Solid Films* **2008**, *517*, 943–947.

(31) Koene, B. E.; Loy, D. E.; Thompson, M. E. Asymmetric Triaryldiamines as Thermally Stable Hole Transporting Layers for Organic Light-Emitting Devices. *Chem. Mater.* **1998**, *10*, 2235–2250.

(32) McEwan, J. A.; Clulow, A. J.; Nelson, A.; Wang, R.; Burn, P. L.; Gentle, I. R. Influence of Dopant Concentration and Steric Bulk on Interlayer Diffusion in OLEDs. *Adv. Mater. Interfaces* **2018**, *5*, 1–10.

(33) Strohriegl, P.; Wagner, D.; Schrögel, P.; Hoffmann, S. T.; Köhler, A.; Heinemeyer, U.; Münster, I. Novel Host Materials for Blue Phosphorescent OLEDs. In *Proceedings of SPIE*; So, F., Adachi, C., Eds.; 2013; Vol. 8829, p 882906.

(34) Walters, D. M.; Antony, L.; de Pablo, J. J.; Ediger, M. D. Influence of Molecular Shape on the Thermal Stability and Molecular Orientation of Vapor-Deposited Organic Semiconductors. *J. Phys. Chem. Lett.* **2017**, *8*, 3380–3386.

(35) Shtukenberg, A.; Freundenthal, J.; Gunn, E.; Yu, L.; Kahr, B. Glass-Crystal Growth Mode for Testosterone Propionate. *Cryst. Growth Des.* **2011**, *11*, 4458–4462.

(36) Powell, C. T.; Paeng, K.; Chen, Z.; Richert, R.; Yu, L.; Ediger, M. D. Fast Crystal Growth from Organic Glasses: Comparison of O -Terphenyl with Its Structural Analogs. *J. Phys. Chem. B* **2014**, *118*, 8203–8209.

(37) Bacchi, A.; Bilotti, I.; Brillante, A.; Crocco, D.; Della Valle, R. G.; Girlando, A.; Masino, M.; Pelagatti, P.; Venuti, E. Raman Investigation of Polymorphism in 1,1,4,4-Tetraphenyl-Butadiene. *J. Raman Spectrosc.* **2013**, *44*, 905–908.

(38) Dračínský, M.; Procházková, E.; Kessler, J.; Šebestík, J.; Matějka, P.; Bouř, P. Resolution of Organic Polymorphic Crystals by Raman Spectroscopy. *J. Phys. Chem. B* **2013**, *117*, 7297–7307.

(39) Musumeci, D.; Powell, C. T.; Ediger, M. D.; Yu, L. Termination of Solid-State Crystal Growth in Molecular Glasses by Fluidity. *J. Phys. Chem. Lett.* **2014**, *5*, 1705–1710.

(40) Fielitz, T. R.; Holmes, R. J. Crystal Morphology and Growth in Annealed Rubrene Thin Films. *Cryst. Growth Des.* **2016**, *16*, 4720–4726.

(41) Stone, K. H.; Schelhas, L. T.; Garten, L. M.; Shyam, B.; Mehta, A.; Ndione, P. F.; Ginley, D. S.;

Toney, M. F. Influence of Amorphous Structure on Polymorphism in Vanadia. *APL Mater.* **2016**, *4*, 76103.

(42) Jones, A. O. F.; Chattopadhyay, B.; Geerts, Y. H.; Resel, R. Substrate-Induced and Thin-Film Phases: Polymorphism of Organic Materials on Surfaces. *Adv. Funct. Mater.* **2016**, *26*, 2233–2255.

(43) Zhang, T. H.; Liu, X. Y. How Does a Transient Amorphous Precursor Template Crystallization. *J. Am. Chem. Soc.* **2007**, *129*, 13520–13526.

(44) Vekilov, P. G. Nucleation. *Cryst. Growth Des.* **2010**, *10*, 5007–5019.

(45) Gower, L. B. Biomimetic Model Systems for Investigating the Amorphous Precursor Pathway and Its Role in Biomineralization. *Chem. Rev.* **2008**, *108*, 4551–4627.

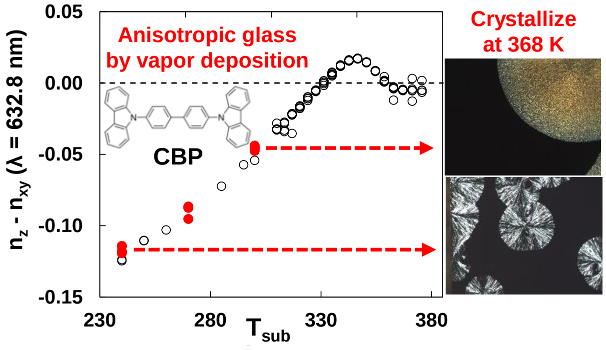
(46) Schmelzer, J. W. P.; Müller, R.; Möller, J.; Gutzow, I. S. Theory of Nucleation in Viscoelastic Media: Application to Phase Formation in Glassforming Melts. *J. Non. Cryst. Solids* **2003**, *315*, 144–160.

(47) Schmelzer, J. W. P.; Zanotto, E. D.; Avramov, I.; Fokin, V. M. Stress Development and Relaxation during Crystal Growth in Glass-Forming Liquids. *J. Non. Cryst. Solids* **2006**, *352*, 434–443.

For Table of Contents Use Only

Glass structure controls crystal polymorph selection in vapor-deposited films of 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP)

Niko Van den Brande, Ankit Gujral, Chengbin Huang, Kushal Bagchi, Heike Hofstetter, Lian Yu, Mark D. Ediger



Anisotropic CBP glasses were prepared by vapor deposition. After eliminating crystal growth at the free surface, these glasses crystallized into either the α or γ polymorph, depending on glass structure. Crystals of both polymorphs grew rapidly below the glass transition temperature T_g compared to previously studied systems. T_g was found to be about 385 K, well above previously reported values.